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ALLENE HYDROCARBONS

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I. INTRODUCTION

Hydrocarbons of the allene series are the least studied class of diolefins although allene and some of its homologues were described in the sixties of the last century[1]†. In recent years research in this field of organic chemistry has expanded considerably. New methods of preparing allenes have been developed and previously known methods improved. The main features of their physical and chemical properties have been made clearer. Promising new ways of converting allenes into various three-, four-, five-, six-, and eight-membered cyclic carbon compounds have been discovered. Compounds with cumulative double bonds are found in nature[2,3].

Allenes apparently play an important part in a number of chemical processes because they are interconvertible with 1,3-dienes and acetylene compounds[4], isolated representatives of which were widely used some time ago in technical as well as in laboratory work.

There is no doubt that a closer examination of the reactions of allenes will provide not only exceptionally interesting new theoretical data but also valuable practical results. The use of various allene polymers in the production of rubber[5,6] and artificial fibres[7] is already reported in a number of patents. Cyanogen adducts of hydroxy--derivatives of allenes are recommended as insecticides[8].

II. METHODS OF PREPARATION

A good review of methods of preparing allenes[9] is available and we shall therefore limit ourselves to very brief descriptions and the most recent publications.

In the earliest researches allene hydrocarbons were obtained by the preferential elimination of halogens of hydrogen halides from polyhalogeno-compounds of suitable structure (the Gustavson method[10]). In particular, allene was prepared as follows:

$$CH_2Br-CHBr-CH_2Br \xrightarrow{KOH} CH_2=CBr-CH_2Br \xrightarrow{Zn} CH_2=C=CH_2.$$

The hydrocarbon yields were not high. Slobodin and Khitrov[11] recently examined this method in detail and showed that the use of butyl or isopentyl acetate as solvent in the elimination of bromine from 2,3-dibromoprop-1-ene raises the hydrocarbon yield to 95–98%, and the allene so obtained is free from the volatile 2-bromopropene impurity which up till now it has not been possible to remove from allene, even with a distillation apparatus of special design[12].

† Allene was first prepared in 1865.[1]

Cyclic allenes with 9, 10, and 11 carbon atoms in the ring were obtained by eliminating hydrogen chloride from 1-chlorocycloalkenes, or halogens from dihalogenocycloalkenes[12,13]. The action of sodamide in liquid ammonia on 1-chlorocycloheptene and 1-chlorocyclooctene gives dimers of the corresponding allenes[13].

The laboratory method which is most widely used at present for the preparation of allene hydrocarbons with a terminal allene group (1,2-dienes) is reduction of halogenoacetylenes or halogenoallenes with a zinc–copper couple in alcohol (Ginzburg method[14,15]), or with lithium aluminium hydride[16]:

$$\left.\begin{matrix} R_2CBr{-}C{\equiv}CH \\ R_2C{=}C{=}CHBr \end{matrix}\right\rbrace \longrightarrow R_2C{=}C{=}CH_2 + R_2CH{-}C{\equiv}CH.$$

(main product)

Allene hydrocarbons are formed with yields of up to 90% by the reduction of various prop-2-ynyl halides, as a result of the acetylene–allene rearrangement[4,17-19]. Reduction of vinylhalogenoacetylenes and halogenodiacetylenes of the same type gives the corresponding vinylallenes and ethynylallenes[20].

The synthesis of monosubstituted allenes by the reaction of prop-2-ynyl bromide with alkylmagnesium bromides, which is also accompanied by the acetylene–allene rearrangement, is particularly simple[21]. The allene hydrocarbons are formed in yields of over 60% and the acetylene hydrocarbons which are formed at the same time are removed as silver acetylide:

$$HC{\equiv}C{-}CH_2Br + C_4H_9MgBr \left\lbrace\begin{matrix} \longrightarrow CH_2{=}C{=}CH{-}C_4H_9 & (65\%)\ddagger \\ \longrightarrow HC{\equiv}C{-}CH_2{-}C_4H_9 & (35\%) \end{matrix}\right.$$

The acetylene–allene rearrangement also takes place in the action of lithium or sodium acetylide on benzyl chloride[22].

Trisubstituted allenes are obtained in very good yields by the action of alkylmagnesium halides on tertiary halides of the prop-2-ynyl type. The reaction complex is decomposed by water from which traces of acid are absent[23].

A new two-stage method of preparing allenes from olefins is very promising. The first stage involves preparation of derivatives of *gem*-dihalogenocyclopropane from olefins and dihalogenocarbene; the second stage is reaction of the dihalide with sodium or magnesium[24,25], lithium alkyls[26,27], or alkyl- or aryl-magnesium halides[28]:

$$\rangle C{=}C\langle + :CBr_2 \longrightarrow \rangle C{-}C\langle \overset{RLi}{\rightarrow} \rangle C{=}C{=}C\langle$$

(with the dibromocyclopropane ring $\rangle C{-}C\langle$ bearing Br_2 on the middle carbon)

The best results were obtained using dibromocyclopropanes and lithium alkyls in absolute ether[27]. From substituted 1,1-dichlorocyclopropanes, a mixture of allenes and alkylcyclopropanes is formed, the yield of the former not exceeding 50%.[26,28]

This method is fairly universal, since by starting with different olefins one can obtain allenes with different structures (aliphatic, alicyclic, and aromatic) in yields of about 70–80%. A disadvantage of the method is that the allene–acetylene rearrangement takes place to some extent in the preparation, and the allenes obtained must be purified from acetylenes.

‡ Total yield 95%.

Formation of allenes by the opening of a three-membered ring also occurs in some other instances, *e.g.* diphenylallene is produced by the action of lithium ethoxide on *N*-(2,2-diphenylcyclopropyl)-*N*-nitrosourea[29].

One of the most convenient methods of preparing symmetrical disubstituted allenes is the addition of lithium alkyls to alkylvinylacetylenes[30].

$$R{-}C{\equiv}C{-}CH{=}CH_2 \xrightarrow{R'Li} R{-}CLi{=}C{=}CH{-}CH_2{-}R' \xrightarrow{H_2O} R{-}CH{=}C{=}CH{-}CH_2{-}R'.$$

The use of divinylacetylene and its homologues in this reaction gives vinylallenes[30,31]. The hydrocarbon yield is about 80%:

$$CH_2{=}CH{-}C{\equiv}C{-}CH{=}CH_2 \xrightarrow{RLi} CH_2{=}CH{-}CLi{=}C{=}CH{-}CH_2{-}R \xrightarrow{H_2O}$$
$$\longrightarrow CH_2{=}CH{-}CH{=}C{=}CH{-}CH_2{-}R.$$

The specific mode of the addition of lithium alkyls is apparently connected with formation of an intermediate complex having the lithium atom attached at the triple bond[32].

The rearrangement of acetylenes on various catalysts, which was studied in detail by Slobodin (on Floridin), in particular, is an equilibrium and gives 1,3-dienes as well as allenes[33,34].

The reaction of prop-2-ynyl halides with arylmagnesium bromides[21,35], the dehydration of some unsaturated alcohols[9], and the prototropic rearrangement of 1,3-arylpropynes over an alkaline alumina catalyst[36] are used to prepare arylallenes.

A mixture of aryl-substituted allenes and arylacetylenes is formed by the chloroarylation of enyne hydrocarbons[37].

Allenes with triphenylmethyl substituents were obtained by the addition of triphenylmethyl free radicals to various enyne hydrocarbons, for example[38,39]:

$$HC{\equiv}C{-}CH{=}CH_2 \xrightarrow{2(C_6H_5)_3C^{\cdot}} (C_6H_5)_3C{-}CH{=}C{=}CH{-}CH_2{-}C(C_6H_5)_3,$$

and also by the classical method of halogenation and dehalogenation of tetraarylethylenes[40].

Information on the preparation of derivatives of allene hydrocarbons containing halogen, oxygen, and nitrogen atoms can be found in Pansevich-Koleda's review[41].

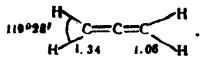
Allenes, like other hydrocarbons, are easily purified chromatographically[42,43]. Melting point curves are recommended as a test for the purity of the preparations[44,45].

III. PHYSICAL PROPERTIES

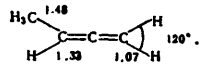
Owing to the two adjacent double bonds, hydrocarbons of the allene series show some peculiarities in their physical properties.

Molecular structure. A stereochemical model of the allene molecule was described by van't Hoff[46]. The three carbon atoms are arranged linearly and the external valencies of the terminal atoms lie in mutually perpendicular planes. Such a structure presupposes the existence of optical isomerism in allenes with two different substituents. Optically active forms of di-α-naphthyldiphenylallene were in fact obtained[47] sixty years after van't Hoff's work. Many examples of optical activity in the allene series are now known[48-51]. Research on the stereochemistry of allenes played an important part in establishing the structure of the natural allenes, mycomycin and isomycomycin[2,3].

Electron-diffraction measurements gave the following parameters for the allene molecule[52,53]:



For methylallene the parameters proposed[54] are:



The central atom in the allene system is in the *sp* state and the outer atoms have sp^2 hybridisation[55].

There are a number of papers on the quantum mechanics and thermodynamics of the allene molecule and its nearest homologues, in which the configuration, symmetry, and energy of the molecule are discussed and thermodynamic constants, many of which feature in the usual handbooks, are given[56–64].

More important constants. From the more important physical constants of allene, and of its homologues and analogues with unsaturated substituents (allyl, prop-2-ynyl, phenyl, naphthyl), given in the Table, the following conclusions can be reached. Allene hydrocarbons usually boil at a higher temperature than paraffins with the same number of carbon atoms and chain structure. As in other homologous series, allene hydrocarbons with the normal structure have higher boiling points than those with a branched chain. Their refractive indices are usually higher than those of the corresponding acetylenes. For the overwhelming majority of known allenes an elevation of the molar refraction of the order of 0.5–1.0 units is observed. The significant discrepancies found possibly indicate inadequate purity of the specimens described. The elevation reaches two units in the conjugated vinylallenes.

The variation of vapour pressure with temperature for allene is given by[82,83]

$$\log P = \frac{0.05233}{T} \times 20.852 + 7.455.$$

There is a definite relation between the boiling point (t_s), specific gravity close to the boiling point (d_s), molecular weight (M), and the number of atoms in the molecule (n)[84]:

$$\frac{t_s}{d_s}\sqrt{\frac{M}{n}} \simeq 1000.$$

TABLE. The more important constants of allene hydrocarbons.

Compound	M.p., °C	B.p., °C	*P*, mm	d_4^t	*t*, °C	n_D^t	*t*, °C	MR_D found	MR_D calc.	Method of preparation*	References
1	2	3	4	5	6	7	8	9	10	11	12
1. Allene and its homologues											
Allene	—136	—34.5	760	0.6575	—30	1.4137	—30	15.30	15.12	I	65,66
				0.7064	—70	1.444	—70				
Buta-1,2-diene	—136.19	10.85	760	0.676	0	1.4205	1.3	20.27	19.74	I	65
				0.652	20						
Penta-1,2-diene	—137.26	44.85	760	0.6926	20	1.4209	20	24.93	24.36	II	65
				0.6876	25	1.4177	25				
Penta-2,3-diene	—125.66	48.26	760	0.6950	20	1.4284	20	25.23	24.36	IV	65
				0.6900	25	1.4251	25				
3-Methylbuta-1,2-diene	—	40	760	0.6800	20	1.4100	20	24.81	24.36	II	65
				0.6759	25	1.4070	25				
Hexa-1,2-diene	—	76	760	0.7140	20	1.4282	20	29.51	28.97	II	66
				0.7102	25	1.4252	25				
3-Methylpenta-1,2-diene	—	70	760	0.715	20	1.4250	20	29.32	28.97	II	65
				0.710	25	1.4220	25				
4-Methylpenta-1,2-diene	—	70	760	0.708	20	1.4240	20	29.55	28.97	II	65
				0.703	25	1.4210	25				
Hexa-2,3-diene	—	68	760	0.6800	20	1.3950	20	28.94	28.97	I	65
				0.6950	25	1.3920	25				
2-Methylpenta-2,3-diene	—	72	760	0.711	20	1.4250	20	29.54	28.97	V	65
				0.706	25	1.4220	25				
Hepta-1,2-diene	—	106	760	0.7374	21	1.4321	21	35.51	33.59	III	21
5-Methylhexa-1,2-diene	—	96	760	0.7225	19	1.4282	19	34.22	33.59	II	67
3,4-Dimethylpenta-1,2-diene	—	—	—	0.751	20	1.4560	20	34.69	33.59	II	19
4,4-Dimethylpenta-1,2-diene	—	80—83	760	0.7184	20	—	—	33.05	33.59	I	33
3-Ethylpenta-1,2-diene	—	97—98	760	0.7423	20	1.4468	20	34.59	33.59	II	14
Hepta-2,3-diene	—	52—53	150	0.7274	20	1.4360	20	34.57	33.59	VI	39
2-Methylhexa-2,3-diene	—	97—100	748	0.7331	20	1.4351	20	34.20	33.59	I	68
2,4-Dimethylpenta-2,3-diene	—	82—84	760	0.7060	20	1.4004	20	33.05	33.59	I	33
Octa-1,2-diene	—	131—132	760	0.7680	15	1.4440	15	38.15	38.21	III	21
3,5-Dimethylhexa-1,2-diene	—	70—71.5	760	0.7435	20	1.4410	20	39.06	38.21	II	19
6-Methylhepta-2,3-diene	—	63—64	100	0.7399	20	1.4380	20	39.03	38.21	VI	39
2,5-Dimethylhexa-2,3-diene	—	119—123	760	0.7637	20	1.4505	20	38.82	38.21	IV	16
Octa-3,4-diene	—	77.5—78	150	0.7443	20	1.4432	20	39.26	38.21	VI	30
3-Methylhepta-3,4-diene	—	30.5	24	—	—	1.4485	18	—	—	III	23
2,2-Dimethylhexa-3,4-diene	—	107.4—108	760	0.7375	25	1.4425	25	39.58	38.21	IV	69
Nona-1,2-diene	—	—	—	0.7581	20	1.4433	20	43.39	42.83	II	19
3-Ethylhepta-1,2-diene	—	145	760	—	—	1.4347	25	—	—	III	70
Nona-2,3-diene	—	64—65	40	0.7555	20	1.4454	20	43.79	42.83	VI	30
2-Methylocta-2,3-diene	—	140—145	744	0.7570	20	1.4370	20	42.91	42.83	I	68
7-Methylocta-2,3-diene	—	62—63	40	0.7525	20	1.4450	20	43.93	42.83	VI	30
6,6-Dimethylhepta-2,3-diene	—	52—53	40	0.7452	20	1.4418	20	44.08	42.83	III	30
Nona-3,4-diene	—	67—68	40	0.7542	20	1.4458	20	43.90	42.83	VI	30
7-Methylocta-3,4-diene	—	60—60.5	40	0.7488	20	1.4430	20	43.98	42.83	VI	30
Deca-3,4-diene	—	82.5—83.5	40	0.7655	20	1.4498	20	48.51	47.45	VI	30
7,7-Dimethylocta-3,4-diene	—	70—70.5	40	0.7555	20	1.4458	20	48.78	47.45	VI	30
2,2-Dimethyldeca-3,4-diene	—	86—87	20	0.7643	20	1.4435	20	57.74	56.68	VI	71
2,2,7,7-Tetramethylocta-3,4-diene	—	74—75	20	0.7645	20	1.4430	20	57.67	56.68	VI	71

TABLE. (contd.)

1	2	3	4	5	6	7	8	9	10	11	12
2. Aliphatic allenes with unsaturated substituents											
Penta-1,2,4-triene	—	46.5—47.5	760	—	—	1.4710	19	—	—	II	20
Hexa-1,2,5-triene	—	73—73.5	760	0.7450	0	1.4480	20	28.74	28.50	III	72
Hepta-1,2,6-triene	—	102	760	—	—	1.4551	24	—	—	V	27
Octa-1,3,4-triene	—	37—38	20	0.7685	20	1.4742	20	39.57	37.74	VI	30
Nona-2,4,5-triene	—	62	20	0.7826	20	1.4856	20	44.80	42.36	VI	73
8-Methylnona-1,3,4-triene	—	70—70.5	20	0.7787	20	1.4690	20	48.72	46.98	VI	30
Deca-1,3,4-triene	—	75—76	20	0.7815	20	1.4742	20	49.01	46.98	VI	30
Undeca-1,3,4-triene	—	91—92	20	0.7841	20	1.4738	20	53.83	51.60	VI	30
Undeca-2,4,5-triene	—	95—96	20	0.7912	20	1.4818	20	54.12	51.60	VI	73
2-t-Butylocta-1,3,4-triene	—	77—78	10	0.7950	20	1.4690	20	57.45	56.63	VI	74
2-t-Butyldeca-1,3,4-triene	—	104.5—106	10	0.8032	20	1.4690	20	66.57	65.45	VI	74
Penta-1,2-dien-4-yne	—	57	760	—	—	1.4850	16	—	—	II	20
Hexa-1,2-dien-5-yne	—	89—90	760	0.798	20	1.4703	20	27.27	26.97	III	72
3. Alicyclic allenes**											
1,1-Pentamethyleneallene	—	52—53	35	0.8503	20	1.4910	20	36.79	36.03	II	19,20
Cyclonona-1,2-diene	—	62	16	0.8914	25	1.5039	25	—	—	V	13,26,27
Cyclodeca-1,2-diene	—	74	10	0.8918	25	1.5071	25	—	—	V	26
Cyclohexadeca-1,2,9,10-tetraene	80	—	—	—	—	—	—	—	—	V	27
4. Allenes with aromatic radicals											
Phenylallene	—	68	16	0.9370	17	1.5830 1.5630	17 20	41.42	39.23	III	21
Benzylallene	—	72—73	17	0.9220	20	1.5460	20	44.64	43.85	III	75
1-Phenylbuta-1,2-diene		44—47 76—77	0.5—1 10	0.9240	26.5	1.5754 1.5698	20 30	46.33	43.85	I	76
5-Phenylpenta-1,2-diene	—	76—77	7	0.9169	20	1.5400	20	49.28	48.45	III	75
2-Methyl-4-phenylpenta-2,3-diene	—	106—108	20	0.9302	20	1.5470	20	53.89	53.08	III	35
3-Methyl-5-phenylhexa-3,4-diene	—	94—95	7	0.9238	20	1.5436	20	58.74	57.70	III	35
1,1-Diphenylallene	—	80	0.1	—	—	1.6301	20	—	—	V	27
1,3-Diphenylallene	49—51	—	—	—	—	—	—	—	—	VII	36
2,2,3-Trimethyl-5-phenylhexa-3,4-diene	—	118—119	10	0.9101	20	1.5335	20	68.25	66.93	III	35
3,4-Diphenylbuta-1,2-diene	—	135—143	760	—	—	—	—	—	—	V	77
3-Methyl-1,1-diphenylbuta-2,3-diene	—	140—150	18	—	—	—	—	—	—	I	122
Triphenylallene	135	—	—	—	—	—	—	—	—	I	78
1-(*p*-Biphenylyl)-3-phenylallene	94.6—95.5	—	—	—	—	—	—	—	—	VII	36
Tetraphenylallene	165	—	—	—	—	—	—	—	—	I	40,79
2,2,6,6-Tetramethyl-3-phenylhepta-3,4-diene	—	78—80	1	0.8808	20	1.5039	20	76.63	76.17	II	80
4,4-Dimethyl-1,1-diphenylpenta-1,2-diene	25—26	115—118	0.55	0.9661	20	1.5690	20	84.09	81.81	II	81

* I) Dehydrohalogenation of halogeno olefins; II) reduction of acetylenic and allenic halides; III) synthesis using organomagnesium compounds; IV) dehydration of unsaturated alcohols; V) *via gem*-dihalogenocyclopropanes; VI) action of lithium alkyls on alkylvinylacetylenes; VII) isomerisation of acetylenes.

** For preparation of allenes with seven- and eight-membered rings, see Refs.12, 27, and 184.

Dipole moments. Only the moments of allene and methylallene (0.4 *D*) have been determined[54,85].

Polarographic data. Allene is reduced at a dropping mercury electrode, the half-wave potential being -2.29 V.[86]

Ultraviolet spectra. Absorption spectra in the ultraviolet are used little in studying hydrocarbons because the absorption usually occurs in the vacuum region. Monosubstituted allenes have an intense band at 1780 Å (Σ 8000) and another at 1880 Å. In the spectra of disubstituted allenes these bands are displaced 30–40 Å towards longer wavelengths and a third band appears at about 2000 Å.[87] Selection rules have been derived for electronic and electronic-vibrational spectra of allenes[88].

Infrared spectra. The problem of identifying different allenes is at present solved mainly by infrared spectroscopy. Allene, its homologues, and derivatives are characterised by an intense band due to asymmetric stretching vibrations of the C=C=C group in the 1950 cm^{-1} region, with some variations depending on the position and nature of substitutents. This band can be used to detect allenes in the presence of other types of dienes and acetylenes[89–96].

When electron-accepting groups are present in the molecule, this band splits into two (at 1930 and 1950 cm^{-1}). Its intensity falls as substitution in allene by electronically similar groups is increased. It is absent from the spectrum of tetraphenylallene, for example; the presence of the allene grouping is demonstrated in this case by nuclear magnetic resonance spectra. If the substituents are of different types they hardly affect the intensity of the band.

The intense band in the 850 cm^{-1} region corresponds to CH deformation vibrations of a terminal allene group. An analogous band appears in the 870 cm^{-1} region of the spectra of symmetrically disubstituted allenes. Different types of allenes can easily be distinguished by these deformation vibration bands.

Raman spectra. There are two intense lines, in the 1100 and 1130 cm^{-1} regions, in the Raman spectra of allene hydrocarbons; their use for analytical purposes has been suggested[89,97–99].

Nuclear magnetic resonance spectra. The chemical shift of the CH_2= group in the spectrum of allene is in a higher-field region than in the spectra of alkenes[100]. The existence of 1,4-spin-spin interaction through the allene

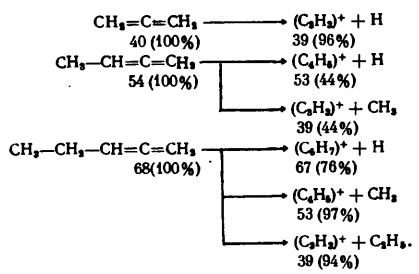
system with constants up to 7 c/s is very characteristic of allene compounds [101,102]. This confirms the *sp* hybridisation of the orbitals of the central atom of the allene system.

Mass spectra. The mass spectra of a number of allenes have been studied in recent years and interesting mechanisms of disintegration of these hydrocarbons under electron impact established [55,103-109].

In the mass spectrum of allene the peak for $(C_3H_4)^+$ ions is the most intense, but that for $(C_3H_3)^+$ ions, which are stabilised either through conjugation or as a result of transition to a cyclic three-carbon ion, is almost as intense. The ionisation potential of allene is 1·2.02 ± 0.03 eV. [55,103]

The highest peak in the mass spectra of methylallene and ethylallene also corresponds to the molecular ions, and the peak for $(C_3H_3)^+$ ions has a high intensity. In methylallene disintegration with loss of hydrogen or methyl to form $(C_4H_5)^+$ or $(C_3H_3)^+$ ions occurs with considerably lesser, and approximately equal, probabilities.

For ethylallene there is approximately equal and high probability of loss of methyl or ethyl higher than of ionisation with loss of hydrogen [55,108].



As the number of carbon atoms in the chain increases, the stability of the molecular ions falls and ions originating through rupture of C–C bonds predominate in the spectra of higher allenes. The formation of many of the fairly intense ions cannot be explained by simple dissociation at one bond; the latter is accompanied either by migration of hydrogen or by simultaneous rupture of two bonds [108,109].

The mass spectra of 2,3- and 3,4-dienes are characterised by specific features which are related to their structure. In 2,3-dienes disintegration to form the most intense ions takes place chiefly at the bond in the β position with respect to the allene system and is accompanied by migration of hydrogen. With 3,4-dienes, however, it occurs mainly at the α bond and without migration of hydrogen. This difference in the dissociative ionisation of allenes can be explained as follows. The ion formed by dissociation of 3,4-dienes achieves the stable prop-2-ynyl structure without migration of hydrogen:

$$R'—CH=C=CH—R \longrightarrow R'—CH=C=CH^+ + R \longrightarrow R'—\overset{+}{C}H—C\equiv CH.$$

whereas on rupture of the β bond of 2,3-dienes stabilisation is possible only with migration of hydrogen.

If the allene system contains a tertiary butyl radical, dissociative ionisation produces mainly $(C_4H_9)^+$ and $(t\text{-}C_4H_9)^+$ ions.

IV. CHEMICAL PROPERTIES

Owing to structural peculiarities, allene hydrocarbons possess specific properties with respect to a number of reagents and therefore occupy a special place among unsaturated compounds.

1. Addition Reactions without Lengthening of the Carbon Chain

Even unsubstituted allene shows unusual features in its addition reactions. Because of its symmetry the molecule is non-polar, but the central atom must be positively polarised with respect to the outer atoms, owing to conjugation and the inductive effect of the C–H bonds.

$$\overset{\delta-}{CH_2}=\overset{\delta+}{C}=\overset{\delta-}{CH_2}.$$

In the reactions of allene with hydrogen halides, water, alcohols, and free radicals, and in diene syntheses, when dipolar-1,3-addition takes place the positions of the added molecules correspond to the formula shown above. However, the course of the addition of mixed halogens, hypohalous acids, and their derivatives does not conform to the polarisation proposed.

The sharp disagreement between the course of addition of halogens and of hydrogen halides is typical only of allenes and is not observed with olefins, acetylenes, or 1,3-dienes. The reason for this can be sought in the geometry of the allene molecule and in the addition mechanism.

It is still more difficult to explain the rules in the addition reactions of allene homologues. They apparently proceed through formation of an intermediate state stabilised above all by hyperconjugation.

Hydrogenation. It is impossible, on the basis of available data on the hydrogenation of allene hydrocarbons in the presence of various catalysts, to reach definite conclusions as to where the first two hydrogen atoms are added. In most cases the hydrogenation was exhaustive and had the aim of establishing the structure of the hydrocarbon. The corresponding saturated compounds were formed in the hydrogenation of allene over palladium [110], 2,4-dimethylpenta-2,3-diene in the presence of platinum [111], tetraphenylallene on boiling with hydriodic acid and phosphorus in glacial acetic acid or by the action of sodium in alcohol [112], and also in the reduction of 1-(*p*-biphenyl)-3-phenylpropadiene under the same conditions [36].

Propene and tetraphenylpropene were obtained by the incomplete hydrogenation of allene [110] and tetraphenylallene [112]. Hexa-1,2-diene was incompletely hydrogenated on nickel to a mixture of hex-1-ene and hex-2-ene with the latter predominating [17]. Hydrogenation of 2-methyl-4-phenylpenta-2,3-diene using sodium in alcohol also gave a mixture of olefins [113].

When symmetrically disubstituted allenes are exhaustively hydrogenated on colloidal palladium, the process takes place at an increasing rate until half the theoretical quantity of hydrogen has been absorbed, after which addition of hydrogen occurs very slowly [114]. The ultimate reduction products are saturated hydrocarbons. The rate of hydrogenation depends on the structure of the hydrocarbons: it increases more rapidly for those with a branched structure. If the process is stopped after absorption of the first mole

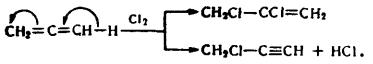
of hydrogen, at the point when the reaction slows down, a mixture of olefins which does not contain the original allene hydrocarbon is isolated§.

Cyclic allenes are easily hydrogenated to cycloolefins on palladium poisoned with pyridine [26].

The heat of hydrogenation of allene to propene at 355°K is 41.265 kcal mole^{-1}, and to propane 71.280 kcal mole^{-1}.[57]

Halogenation. The available data on halogenation relate mainly to allene and some of its simplest homologues.

When allene is chlorinated in chlorine-containing solvents, 2-chloropropene and prop-2-ynyl chloride are formed in equimolar quantities. The latter is a primary product of the reaction and is not formed by elimination of hydrogen chloride from 2,3-dichloropropene under the conditions used[115]:



When allene is brominated in acetic acid in the presence of potassium bromide, addition of rather more than one mole of bromine takes place rapidly, and then the reaction becomes very slow. The action on allene of solutions of iodine chloride in acetic acid and carbon tetrachloride is similar[115]. Complete bromination of allene is achieved by the bromide–bromate method[116], and also with bromine in chloroform[10].

2-Bromo-3-chloroprop-1-ene is formed by the action of bromine chloride on allene, *i.e.* the central atom in allene displays negative polarisation[115].

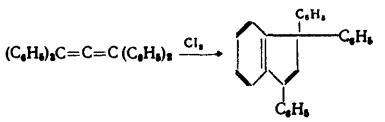
Addition of bromine to methylallene gave 2,3-dibromobut-1-ene, which easily isomerises even at room temperature to 1,2-dibromobut-2-ene[117]. Complete bromination gave 1,2,2,3-tetrabromobutane[33].

Bromination of ethylallene and propylallene also takes place at the substituted double bond to form respectively 2,3-dibromopent-1-ene and 2,3-dibromohex-1-ene, and then the tetrabromides[67,117,118]. Unsymmetrical dimethylallene is brominated to 3,4-dibromo-2-methylbut-1-ene which is capable of the allylic rearrangement to 1,2-dibromo-3-methylbut-2-ene[118]. The latter dibromide was obtained in earlier work, apparently because the possibility of a rearrangement was not considered[119,120]. Bromination of 1-phenylbuta-1,2-diene gives 2,3-dibromo-1-phenylbut-1-ene[76].

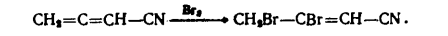
The addition of halogens preferentially at the more substituted double bond is possibly explained by the latter's high polarisation under the influence of the $+I$ effect of the radicals.

Addition of bromine to symmetrically disubstituted allenes occurs preferentially at the bond which is further removed from the end of the molecule. 3,4-Dibromopent-2-ene was obtained from symmetrical dimethylallene[76].

Phenyl radicals in the molecule reduce the rate of bromination considerably. Tetrabromides were, however, obtained from phenylallene, phenyltrimethylallene, and methyldiphenylallene[113,121,122]. Bromine is added with difficulty to triphenylallene[78], and indenes are formed by the action of halogens on tetraphenylallene[112]:



Addition of halogens (chlorine or bromine) to allenes containing electronegative groups takes place at the unsubstituted double bond, for example[123]:



Addition of hydrogen halides. Whereas in halogenation of allenes the two possible monoadducts are interconvertible by the allylic rearrangement and the discrepancies between the results of different authors can be explained by small changes in the conditions of preparation or treatment of the reaction products, in the addition of hydrogen halides only two of the four possible adducts can be interconverted by the allylic rearrangement. The published data here indicate reliably that there are fundamental differences in the course of addition, depending on the structure of the allene hydrocarbons.

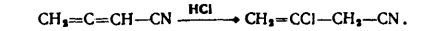
With hydrogen fluoride allene forms 2,2-difluoropropane, and with hydrogen chloride 2-chloroprop-1-ene and 2,2-dichloropropane[124,125]. The addition thus obeys Markovnikov's rule.

Addition of hydrogen chloride to methylallene (giving 2-chlorobut-2-ene and 2,2-dichlorobutane)[125] and propylallene (giving 2-chlorohex-2-ene and 2,2-dichlorohexane) in the presence of bismuth trichloride[17] is similar.

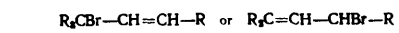
With unsymmetrical dimethylallene addition of hydrogen chloride occurs in a different way, mainly 3-chloro-3-methylbut-1-ene being formed. The ratio of the allylic isomers is 64 : 36.[125] When hydrogen chloride is added to homologues of allene partial isomerisation to 1,3-dienes takes place.

In earlier work it was suggested that 1-chloro-3-methylbut-2-ene is formed on addition of hydrogen chloride to dimethylallene[126]. Allylic rearrangement evidently occurs under the conditions of the reaction.

Addition of hydrogen chloride to allenes with electronegative substituents takes place at the substituted double bond[123]:



Addition of hydrogen bromide to allenes proceeds in the same way: the peroxide effect was not observed. Ethylallene gives 2-bromopent-2-ene and also 2-bromopent-1-ene and 2,2-dibromopentane[67,127], propylallene gives 2-bromohex-2-ene and the corresponding dihydrobromide[118], and unsymmetrical dimethyl-, diethyl-, and trimethyl-allenes give, depending on the conditions, one or two linked hydrobromides, interconvertible by the allylic rearrangement:



and also dihydrobromides with bromine atoms in the 1,3-positions[118,128,129]. The latter are often used for the synthesis of cyclopropane hydrocarbons[130].

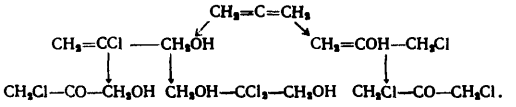
§ When disubstituted allenes are hydrogenated by the action of lithium or sodium in liquid ammonia, mainly alk-2-enes are formed[185].

In the electrophilic addition of hydrogen halides the proton attacks the outer carbon atoms in the case of alkylallenes and the middle carbon atom in the case of unsymmetrical dialkylallenes. Evidently in the two cases the intermediate ion is formed which is the more stabilised by hyperconjugation.

Hydrogen chloride and hydrogen bromide are added to symmetrically disubstituted allenes to form a mixture of hydrobromides in which the hydrogen is attached both to the outer and to the middle carbon atoms of the allene system [118].

Tetraphenylallene gives with hydrogen halides dark unstable products [112].

Addition of hypohalous acids and their esters. The action of hypochlorous acid on allenes was studied long ago but only in two cases. Mainly a chloro--keto-alcohol (3-chloro-1-hydroxypropan-2-one), dichloroacetone (15%), and chloroallyl alcohol (10%) were obtained from allene [131].



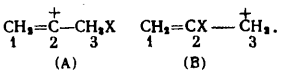
The addition of hypochlorous acid to unsymmetrical dimethylallene was even more complex, giving a mixture of products from which were isolated in the largest amounts a chloro-keto-alcohol (1-chloro-3-hydroxy-3-methylbutan--2-one), a dichloro-ketone (1,3-dichloro-3-methylbutan-2--one), and a dichloro-glycol (2,2-dichloro-3-methylbutane--1,3-diol). [131] The first and last products are assumed to be formed through intermediate products of the following structures:

$$(CH_3)_2COH{-}CCl{=}CH_2 \text{ and } (CH_2)_2C{=}CCl{-}CH_2OH,$$

which are produced by addition of one molecule of hypochlorous acid. Thus in both cases addition of hypochlorous acid to the allene system took place contrary to Markovnikov's rule, *i.e.* differently from the addition of other electrophilic reagents.

Combined hypobromination by the action of bromine and methanol on allenes also mainly occurs contrary to Markovnikov's rule [76].

Addition of electrophilic reagents to allene may be accompanied by formation of two types of ion in the transition state:



At the time when ion B is formed in the transition state conjugation cannot take place because the positive charge and the electron pair are in different planes. In order to achieve conjugation, atom C_3 must be rotated about the C_2-C_3 axis, which requires expenditure of energy. Ion A is stabilised through hyperconjugation. Ion B is consequently not always more stable than ion A and it is, in principle, possible for either to be formed. Comparison of the reactions described above suggests that the reactions which are accompanied by considerable heat usually occur through formation of ion B. It is possible that in reaction complexes which are richer in energy, conditions obtain for achieving conjugation and ion B is more favoured.

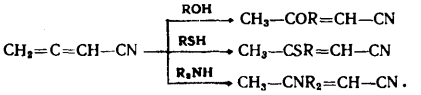
Addition of water, alcohols, acids, and their sulphur analogues. Hydration of allene and its homologues which have one or two radicals attached to the cumulative bond system occurs easily by the action of 80% sulphuric acid or under the conditions of the Kucherov reaction, only ketones being formed [10,17,28,67,132,133].

Water is added, irrespective of the structure of the allene, in strict accordance with Markovnikov's rule. The ease of hydration distinguishes allenes from other dienes; in this respect they are more like acetylenes.

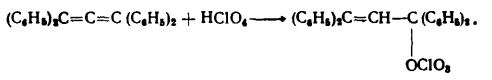
Research on the reactions of allene hydrocarbons with alcohols in the presence of alkali formed part of the major research carried out by Favorskii and his students on the isomeric rearrangements of hydrocarbons of the C_nH_{2n-2} series [134]. Addition of an alcohol in the presence of alkali is possible with allenes, as with acetylenes, but not with olefins and dienes with conjugated or isolated double bonds. This is due to the special "acetylenic" nature (*sp* hybridisation) of the central atom of the allene system. The reaction is usually carried out by heating to 150–170°. Allene gives ethyl isopropenyl ether. Methylallene and symmetrical and unsymmetrical dimethylallenes isomerise under these conditions to disubstituted acetylenes. t-Butylallene is unchanged [120,135-137].

Addition of alcohols to allenes in the presence of boron trifluoride and mercuric oxide, studied using propylallene, follows the same path, with formation of acetals [17].

Addition of alcohols, mercaptans, and amines to allenes containing electronegative substituents takes place at the unsubstituted double bond [123]:



The addition of perchloric acid to tetraphenylallene occurs in a different way [138]:



This reaction needs further study.

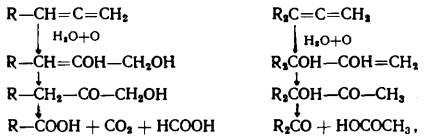
The crystalline addition products of 2,4-dinitrobenzenesulphenyl chloride and cyclic allenes have been used for identification of the latter [26].

Addition of peroxide compounds and oxidative cleavage.

(a) Action of potassium permanganate solutions. Many allene hydrocarbons have been oxidised using potassium permanganate with the aim of establishing their structures. Although the glycols (or rather keto-alcohols) which are first formed were not isolated, it is nevertheless possible to judge from the reaction products to which of the double bonds the elements of hydrogen peroxide were added first.

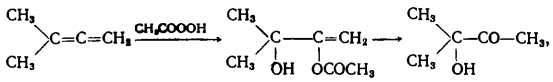
In the oxidation of monosubstituted allenes (t-butyl- and phenyl-allenes) formic acid was obtained, but not acetic acid; this indicates that the oxidant acts first at the outer double bond [113,121,139]. With unsymmetrically disubstituted

allenes (dimethylallene) it is the double bond at the most substituted carbon atom which undergoes oxidation, since acetic acid is a reaction product [14,140]. With trimethylallene the oxidation products agree with both possible modes of oxidation [140].

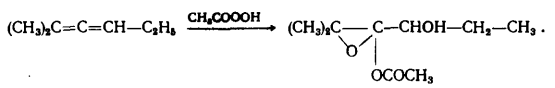


(b) Action of ozone. Ozonisation of allenes has also been studied only as a means of demonstrating their structures. The formation of a monoozonide has never been recorded and it is therefore impossible to draw conclusions as to the way in which ozone is added to allenes [33,121,140].

(c) Action of hydroperoxides. Addition of hydroperoxides either takes place at the more substituted double bond as, for example, in the reaction of unsymmetrical dimethylallene with acetyl hydroperoxide:



or acts at both bonds forming epoxides of glycol esters [141]:



Pansevich-Koleda has examined this reaction in detail [68], and has reviewed the subject [41].

(d) Action of lead tetraacetate. This reaction has been studied for a few hydrocarbons, but the mode of addition of the acetoxy-group has not been proved rigorously [142].

(e) Addition of the elements of hydrogen peroxide to ethylallene by the action of an aqueous solution of silver perchlorate on ethylallene in the presence of osmium tetroxide took place at the more substituted double bond [143].

Addition of alkyldichlorosilanes. The mode of addition of methyldichlorosilane to propyl-, butyl-, methylpropyl-, methylpentyl-, and ethylpropyl-allenes and of ethyldichlorosilane to propyl- and butyl-allenes in the presence of chloroplatinic acid has been investigated. The silicon-containing chlorides obtained were alkylated with methyl- or ethyl-magnesium bromide without being isolated [144].

Silylolefins of the type $R-CH=CH-CH_2-SiR_3$ were obtained by the addition of methyl- or ethyl-dichlorosilanes to monosubstituted allenes. Disubstituted allenes gave mainly adducts with a silyl group at the smaller radical.

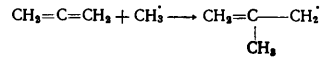
The mode of addition of alkyldichlorosilanes to allenes was thus found to be different from that for the addition of water or hydrogen halides. The results obtained are best explained by a radical mechanism for the reaction.

Addition of nitrogen trioxide. Allene gives a pseudonitrosite with nitrogen trioxide [145].

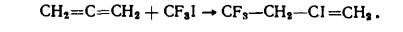
2. Addition Reactions with Lengthening of the Carbon Chain

Addition of free radicals. Divinyl hydrocarbons are the most reactive towards free radicals. This is explained by the high stability of the allyl radicals formed.

Addition of the methyl radical, which is nucleophilic, to allene takes place more slowly than to dienes or even to olefins. Substitution of the hydrogen atoms of allene by alkyl or phenyl radicals has little effect on the reactivity of the allene system. In this respect allenes differ markedly from conjugated dienes and olefins, the reactivity of which towards methyl radicals depends very much on the position and nature of the substituents. The lack of relation between the rate of reaction and the type of substituent indicates that only the central atom of the allene system undergoes attack [146].



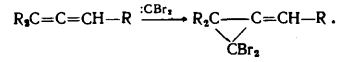
Addition of the electrophilic trifluoromethyl radical occurs only at the outer carbon atoms of allene. Thus allene and CF_3I gave, by a radical reaction, 1,1,1-trifluoro-3-iodobut-3-ene: [147]



Radicals thus behave towards the allene system in the same way as hydrogen halides. In reactions with radicals and hydrogen halides a higher electron density is found on the outer carbon atoms of the cumulative system.

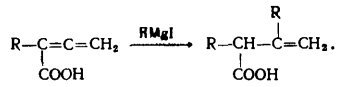
Methylene radicals, produced in the photolysis of ketene and diazomethane, form methylenecyclopropane and methylallene with allene [148].

It was shown recently that addition of dibromocarbene to allene hydrocarbons occurs at the most substituted double bond [149,150]:



This reaction provided a new method of synthesising derivatives of methylenecyclopropane which is difficult to prepare in other ways.

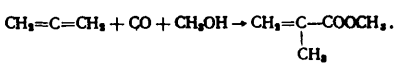
Addition of organometallic compounds. There are no published data on the mode of addition of organometallic compounds to allene hydrocarbons. The addition of alkylmagnesium halides to allene acids takes place at the double bond which carried the carboxy-group [151,152]:



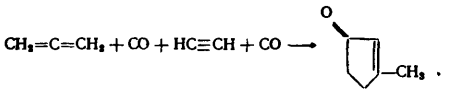
These acids do not react as dienophiles and polymerisation can occur [153].

Reaction with carbon monoxide. Like acetylene, allene adds on carbon monoxide in the presence of metals which are able to form carbonyls (ruthenium). Water, alcohols, ammonia, amines, or acetylene can be used as the second component [154].

Methyl methacrylate was obtained from allene, carbon monoxide, and methanol:



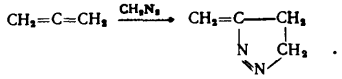
Acetylene, carbon monoxide, and allene gave 3-methylcyclopent-2-en-1-one:



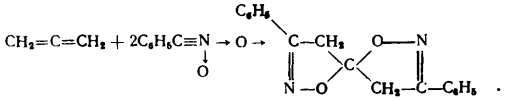
Allene hydrocarbons which have a hydrogen atom in the position α to the cumulative bonds (allene, butylallene, etc.) can react with cobalt carbonyl at room temperature with liberation of carbon monoxide and formation of organometallic complexes which cause polymerisation of the original hydrocarbon[155].

Reaction with tetranitromethane. Allenes, like other unsaturated compounds, give yellow products with tetranitromethane. Introduction of a phenyl radical into the molecule deepens the colour while a t-butyl radical makes it paler. The nature of the products has not been determined[156].

Dipolar 1,3-addition also produces lengthening of the carbon chain. With diazomethane allene forms methylenepyrazoline but the position of the substituent has not been established precisely[157]:

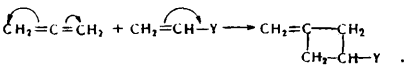


Benzonitrile oxide is added to both double bonds of allene to form 3,3'-diphenyl-5,5'-spirobi-(4*H*,5*H*-isoxazoline)[158]:



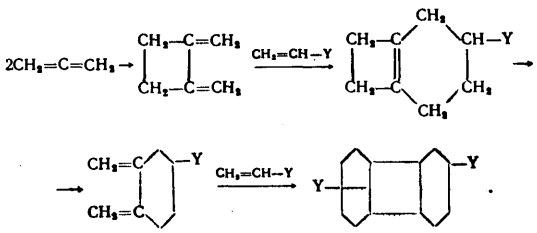
3. "Ene" and Diene Synthesis

Allene hydrocarbons are involved in diene synthesis as dienes and dienophiles. Allene and a number of its homologues give cyclobutane-type condensation products with many typical dienophiles (maleic anhydride, acrylonitrile and methacrylonitrile, methyl acrylate and methyl methacrylate, methacrylic aldehyde, itaconic ester, α-methylstyrene, etc.) by the following mechanism (for allene)[159-161]:

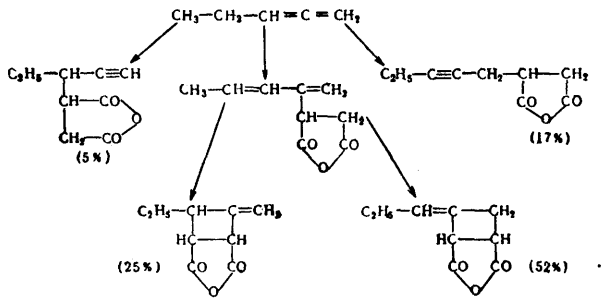


Derivatives of octalin and acetylene compounds are formed as by-products.

The formation of octalin derivatives is explained by partial dimerisation of allenes under the conditions of the reaction. The dimers then take part in diene synthesis in the usual way:



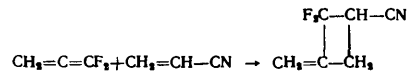
The formation of acetylene compounds indicates an unusual mechanism for the condensation of allenes with dienophiles. The reaction evidently occurs not by "diene", but by "ene" synthesis. For example, condensation of ethylallene with maleic anhydride gives products corresponding to all three possible paths for "ene" synthesis:



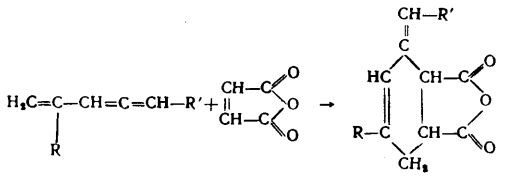
Addition of maleic anhydride occurs at both double bonds but the outer double bond is more than twice as reactive as the middle bond.

With tetrafluoroethylene allene gives methylenetetrafluorocyclobutane and spirobistetrafluorocyclobutane[162].

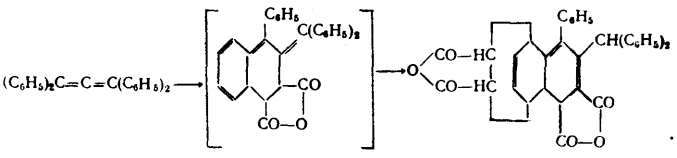
Condensation of difluoroallene with dienophiles takes place at the substituted doubled bond[163]:



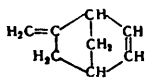
Vinylallene and its homologues can be condensed with maleic anhydride at the 1,3-conjugated system to form substituted methylenecyclohexenes[20,74]:



Phenyl-substituted allenes behave differently from aliphatic allenes in that two molecules of maleic anhydride are added to them to give derivatives of phenylnapthalene[164].

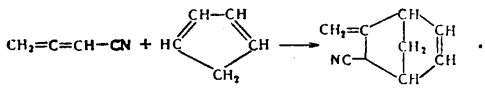


Allenes react as "dienophiles" with 1,3-dienes; for example, with cyclopentadiene the following adduct is formed[165]:



as well as derivatives of naphthalene and anthracene and products of further addition of cyclopentadiene to this adduct.

Condensation of allene nitriles with cyclopentadiene takes place at the substituted double bond[123]:



4. Polymerisation of Allenes

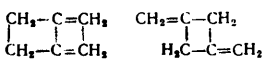
The ability to polymerise on heating is characteristic of allenes to no less an extent than of dienes with conjugated double bonds. The principal features of the thermal polymerisation of allenes were established by Lebedev for allene, symmetrical and unsymmetrical dimethylallenes, and trimethylallene[166].

In contrast to 1,3-dienes, allenes polymerise on heating at almost identical rates, irrespective of structure. The rate constants for the polymerisation of three of the allenes mentioned above were calculated by Gapon[167] from Lebedev's data. This feature [identical rates (Ed. of Translation)] indicates that at the beginning of the polymerisation process two hydrocarbon molecules combine through the two central carbon atoms.

A distinctive feature of the allene type of polymerisation is also the formation of a continuous series of compounds containing cyclobutane rings, from dimer to hexamer and beyond.

The process is complicated by polymerisation of a type characteristic of 1,3-dienes, owing to partial isomerisation of allenes to 1,3-dienes on heating.

In the case of allene, dimers, trimers, tetramers, pentamers, and hexamers have been isolated. The dimer is a mixture of the following two substances:

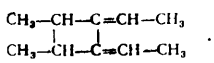


the former predominating[168,169].

The tetramer is also obtained in two forms, one of which is produced by condensation with transition to a divinyl structure.

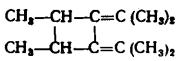
At 500–550° methylallene gives mainly a mixture of dimers together with gaseous hydrocarbons (methane, ethane, ethylene, propene, allene, and methylacetylene)[170].

Only one dimer and one trimer are obtained from symmetrical dimethylallene:



Unsymmetrical dimethylallene gives the two possible dimers. Only one trimer with a definite structure was isolated from a mixture of trimers[171].

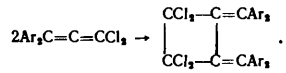
One dimer, which makes up 90% of the crude polymer, was obtained from trimethylallene:



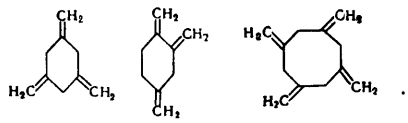
Allenes with seven- and eight-membered rings can polymerise to dimers under the action of alkali[26].

Fluorinated allenes also give dimers containing a cyclobutane ring. 1,2-Bis(difluoromethylene)tetrafluorocyclobutane was obtained from tetrafluoroallene[172], and 2-difluoromethylene-1-methylenedifluorocyclobutane from 1,1-difluoroallene[163]:

Diaryldihalogenoallenes form four-membered rings through the halogen-substituted bonds[173]:

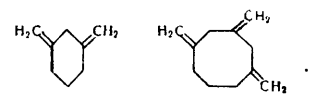


A new type of cyclopolymerisation of allene in the presence of nickel complexes which gives polymers containing six- and eight-membered rings was discovered recently[174]:



This type of trimerisation indicates the similarity between the structures of allene and acetylene.

It is of interest that in the presence of nickel catalysts allene enters into joint cyclopolymerisation with acetylene hydrocarbons (acetylene, and methyl-, phenyl-, and vinyl-acetylenes) in the ratios 2 : 1 and 3 : 1, with formation of six- and eight-membered rings, *e.g.* for allene[174]:



Photopolymerisation of allene[175] and polymerisation under the action of radon[176] have also been investigated.

5. Isomeric Rearrangement of Allenes

Since the discovery of the allene–acetylene–1,3-diene rearrangement the interconversion of acetylenes and dienes has been the subject of innumerable researches. Allene hydrocarbons can isomerise in three ways: to monosubstituted acetylenes, to disubstituted acetylenes, or to conjugated dienes.

Conversion of allenes into monosubstituted acetylenes is easily achieved by heating with sodium metal or sodamide[10,67,111,135,137,139]. In this case the isomerisation is irreversible because the monosubstituted acetylene is removed from the reaction as the sodium derivative.

The use of other catalysts (Floridin, metal oxides) allows this reaction to be carried out reversibly, as has been demonstrated for allene, methylallene, and unsymmetrical dimethylallene[33,34]. The allene–methylacetylene equilibrium constant depends only on temperature[34].

Conversion of allenes into disubstituted acetylenes takes place when they are heated with alcoholic alkali[25,120,135-137], and into conjugated dienes under the action of various catalysts and at an elevated temperature[33,34,98,177-182]. The heat of isomerisation of buta-1,2-diene to divinyl is 12.78 ± ± 0.16 kcal mole^{-1}.[177] Floridin, metal oxides, and halide salts of quinoline were used as catalysts.

Cyclic allenes can isomerise to 1,3-dienes under the action of alkali[26].

Isomeric rearrangements of allenes involve, in all probability, removal of a proton by the base and its addition to another part of the molecule[183].

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MECHANISM OF THE OXIDATIVE THERMAL DEGRADATION AND OF THE STABILISATION OF POLYMERS

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1. OXIDATION IN GAS AND LIQUID PHASES

After Bakh[1] and Engler[2] had formulated the peroxide theory of oxidation, many papers appeared on the oxidation of hydrocarbons and other organic compounds. Many oxidations were found to be autocatalytic and characterised by well-defined induction periods. Work in this field entered a new phase of development with the theory of chain branching[3], and especially the theory of degenerate explosions[4]. The principal results obtained on oxidation were generalised on the basis of the theory of chain reactions[5]. Under the influence of the work done by the Semenov and Hinshelwood schools, a great deal of research effort was devoted to the mechanism of the oxidation of organic compounds in the gas and liquid phases.

Shortly afterwards it was suggested that the main task of research in this field was to determine the rate constants of the elementary reactions in a complicated radical-chain

process of oxidation, so that the rate of oxidation could be calculated from its hypothetical mechanism. Comparison of the experimental results with theoretical calculation would enable the correctness of the proposed mechanism to be assessed. Recent monographs by Semenov[6] and by Kondrat'ev[7] have summarised the progress achieved on these lines.

The most important results were obtained in investigations of gas-phase oxidations. Nalbandyan and Voevodskii based a radical–chain scheme for the oxidation of hydrogen on published data and their own results, and showed that all deductions made from this scheme agreed well with experiment[8]. Values of many of the constants adopted in this work have now been verified and refined[9].

The development of the electron paramagnetic resonance (EPR) method has permitted the experimental detection of several free radicals and atoms formed in the course of oxidation, and has thus yet again confirmed the correctness of the accepted schemes for the oxidation of hydrogen and of several other substances. It has been demonstrated that hydrogen atoms[10,11], oxygen atoms[12], and $HO_2^{\cdot}$ radicals[13] are formed in the oxidation of hydrogen.

Semenov and his coworkers, having set up a scheme for the oxidation of methane, used published values for the rate constants of the elementary reactions to calculate the maximum concentration of formaldehyde formed in this process[6]. The result differed from the experimental value by less than an order of magnitude, which must be regarded as good agreement, since only rough values were known for many of the rate constants used in the calculations.

Matters are considerably worse than in the gas phase for research on the mechanism of oxidation in the liquid phase. In spite of the large amount of work done in this field, the results of which have been surveyed in several reviews[14-18], it has not yet proved possible to solve the problem of constructing from elementary reactions a mechanism for even the simplest liquid-phase oxidations of organic compounds. Therefore work on the elementary processes occurring in the liquid phase and on determining their rate constants becomes of great importance[19,20].

The development of work in this field has been considerably accelerated by the application of new methods of investigation. Much new information has been obtained, for example, by the use of labelled atoms, especially by the kinetic tracer method[21]. This method has yielded the sequence in which various intermediate products are formed in the oxidation of cyclohexane and other hydrocarbons, and has also yielded the rates of formation and consumption of the intermediate products[22,23]. The relative rates of several liquid-phase radical reactions have been determined by means of labelled atoms[24-27].

Chemiluminescence provides a promising method[28] of investigating the rates of several radical reactions in the liquid phase, and has recently been successfully employed to prove that $R^{\cdot}$ and $RO_2^{\cdot}$ radicals are involved in the liquid-phase oxidation of hydrocarbons[29]. It has made possible assessment of the competition between the reactions

$$R^{\cdot}+O_2 \xrightarrow{k_1} RO_2^{\cdot},$$

and

$$R^{\cdot}+R^{\cdot} \xrightarrow{k_3} RR,$$

and evaluation of the ratio $k_1/\sqrt{k_2}$ for the oxidation of ethylbenzene at 60°, for which 2.7×10^4 litre$^{1/2}$ mole$^{-1/2}$ sec$^{-1/2}$ has been obtained.

By means of the chemiluminescence method it has been possible to measure the absolute rates of several oxidations, the efficiencies of various initiators, and rate constants for reactions between radicals and several antioxidants. The immense prospects of developing this method for the investigation of oxidation mechanisms in liquid and solid phases are easily visualised.

Among other methods, polarography was first employed to determine peroxides and aldehydes formed in the oxidation of hydrocarbons[30]; while chromatography has been widely used for kinetic investigations in gas, liquid, and solid phases[31].

Rates of initiation and chain branching in liquid-phase oxidations are often determined by the so-called inhibitor method, in which the rate of consumption of an inhibitor is measured[32]. The weak points in this method have been discussed[33,34].

The mechanism of the radical–chain oxidation of n-decane has been investigated in very great detail[35-39]. On the basis of this and the work of other investigators it can now be assumed that the most probable scheme for the oxidation of a hydrocarbon RH in the liquid phase is as follows:

$$RH+O_2 \xrightarrow{w_i} R^{\cdot}+HO_2^{\cdot}.$$

A termolecular initiation reaction[40] is also possible, since it is less endothermic:

$$2RH+O_2 \longrightarrow 2R^{\cdot}+H_2O_2.$$

The chain reaction is then propagated as follows:

$$R^{\cdot}+O_2 \xrightarrow{k_1} RO_2^{\cdot},$$

$$RO_2^{\cdot}+RH \xrightarrow{k_2} ROOH+R^{\cdot}.$$

Chain termination takes place by the recombination of radicals:

$$\left.\begin{aligned} RO_2^{\cdot}+RO_2^{\cdot} &\xrightarrow{k_3} \\ R^{\cdot}+R^{\cdot} &\xrightarrow{k_3'} \\ R^{\cdot}+RO_2^{\cdot} &\xrightarrow{k_3''} \end{aligned}\right\} \text{inactive products}.$$

Degenerate branching occurs as a result of breakdown of the hydroperoxide:

$$ROOH \xrightarrow{k_4} RO^{\cdot}+OH.$$

The sector method[41] has yielded values of the rate constants k_1-k_4 and the rate of initiation w, which has made it possible to calculate the rate of the complicated reaction in the early stages of oxidation, when no products other than the hydroperoxide play a significant part.

Since the values of the constants depend on the structure of the radical $R^{\cdot}$, and the mechanism of the process changes as active reaction products accumulate, it is clear what a large amount of work must first be done before it is possible to solve the problem of determining the mechanism of a liquid-phase oxidation from the elementary reactions.

2. OXIDATION IN THE SOLID PHASE

Investigations of the mechanism of oxidation in the solid phase, in particular of the oxidation of polymers, are in a still worse situation. Work in this field has begun comparatively recently.

Since polymers are obtained from monomers belonging to different classes of organic compounds, they differ among themselves not only in the fine mechanisms of oxidation but even in the character of the overall processes. In the oxidation of poly(vinyl chloride), for example, an important part is played by the elimination of HCl molecules and the formation of double bonds. The oxidation of polyamides takes place without an appreciable induction period, and differs markedly in character from the oxidation of hydrocarbons. The oxidative thermal degradation of polysiloxanes is also distinctive. Condensation polymers — epoxide resins, polyarylates, and polycarbonates — begin to oxidise at comparatively high temperatures. The oxidation of unvulcanised and vulcanised rubbers is also very characteristic.

Let us consider results obtained for the oxidation of polypropylene, since the process has been investigated in the greatest detail for this polymer, and its mechanism is very close to that of the liquid-phase oxidation of hydrocarbons.

The EPR method has shown the formation of two types of radicals — alkyl $RCH_2\dot{C}HCH_2R$ and allyl $RCH_2\dot{C}HCH{:}{:}CHCH_2R$ — in polyolefins on exposure to γ-rays or fast electrons. It may be assumed that radicals of the allyl type are formed by the reaction of alkyl radicals with macromolecules containing double bonds[42]. The EPR method has also shown that radicals R in polymers can add on oxygen to form peroxy-radicals $RO_2^{\cdot}$.[43]

The sector method has been used[44,45] to study the oxidation of 2,4,6-trimethylheptane, a model compound for a segment of the polypropylene molecule. The light-initiated oxidation took place by the radical–chain mechanism

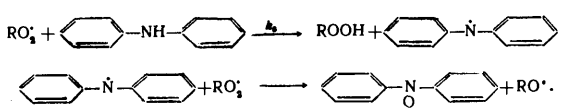
$$RH+h\nu \xrightarrow{w_i} R^{\cdot},$$

$$R^{\cdot}+O_2 \xrightarrow{k_2} RO_2^{\cdot},$$

$$RO_2^{\cdot}+RH \xrightarrow{k_3} ROOH+R^{\cdot},$$

$$RO_2^{\cdot}+RO_2^{\cdot} \xrightarrow{k_4} \text{inactive products}.$$

Chain termination on the addition of diphenylamine is represented by



Values of all the elementary reaction constants were determined over the temperature range 6–80°. Application of the EPR method showed the formation of a stable diphenylnitric oxide radical.

The EPR method has shown the formation of a peroxide radical in the oxidation of ethylbenzene[46], and the rate constants of recombination of the radical have been determined.

3. OXIDATION OF POLYPROPYLENE

Isotactic polypropylene and other polyolefins oxidise by a radical–chain mechanism with degenerate branching. This is indicated by the presence of a well-defined induction period and the autocatalytic character of the reaction, which obeys the law $w = Ae^{\varphi t}$. Branching takes place at hydroperoxides[47]. Addition of a peroxide to the polymer shortens the induction period in proportion to the square root of its concentration, which indicates the occurrence of quadratic chain termination.

The accumulation of peroxides in the oxidation of atactic polypropylene has been studied, and the effective activation energy of formation of several of its oxidation products has been determined[48,49].

In a more detailed investigation of the kinetics of the oxidation of isotactic polypropylene[50] volatile degradation products were frozen out in traps cooled in solid carbon dioxide, and among them were detected water, formaldehyde, acetaldehyde, acetone, methanol, hydrogen peroxide, carbon dioxide, and hydrogen. The aldehydes and the hydrogen peroxide were determined polarographically, and other products by gas and gas–liquid chromatography. Fig. 1 shows one of the chromatograms obtained. The hydroperoxide formed in polypropylene was determined iodometrically. The accumulation of C:O and OH groups was followed by means of the infrared absorption spectra.

Fig. 2 shows the oxygen absorption curve obtained in an experiment at 130° and an oxygen pressure of 400 mm. The maximum rate of absorption of oxygen corresponds to the oxidation of 15% of the monomer units in the polymer. At the same instant the peroxide concentration also reaches a maximum. During the first 50 min of oxidation almost the whole of the absorbed oxygen is present as hydroperoxides.

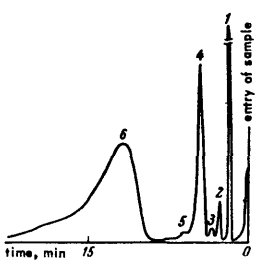


Fig. 1. Chromatogram of volatile products obtained in the oxidation of isotactic polypropylene:
1) H_2 + CO; 2) CH_3CHO; 3) unidentified; 4) CH_3COCH_3; 5) unidentified; 6) H_2O.

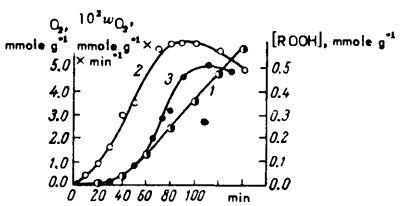


Fig. 2. Oxidation of polypropylene at 130° and p_{O_2} = 440 mm:
1) absorption of oxygen; 2) rate of absorption of oxygen; 3) accumulation of peroxides.

Calculation based on the results of several series of experiments showed that the rate of absorption of oxygen was proportional to $[RH]^{3/2} \times [ROOH]^{1/2}$. This conclusion is confirmed by Fig. 3, in which the experimental results are plotted as $w_{O_2}/([RH] \times [ROOH])$ against $([RH]/[ROOH])^{1/2}$. The concentration [RH] was taken to mean the number of unoxidised tertiary carbon atoms in 1 g of polymer. It was assumed that not more than one molecule of oxygen added on to each monomer unit.

Determinations were also made of the rates of formation of water, acetone, aldehydes, hydrogen peroxide, and methanol. Fig. 4 shows the rate curves for the formation of water and acetone, those for the other products being of the same form. The curves for acetone, aldehydes, and hydrogen peroxide can be compared with that for water by changing the velocity (vertical) scale, as shown in Fig. 5. In this way the relation between the rates of formation of the various products during the process is unaffected.

It may be supposed that all secondary products are formed by breakdown of the primary oxidation products, which are the hydroperoxides. The experiments showed that the rate w of formation of water and the other substances was proportional to the product [ROOH] × [RH], as is evident from Fig. 6. This confirms the suggestion that all the substances formed result from decomposition of a hydroperoxide. The proportionality of the rate to the

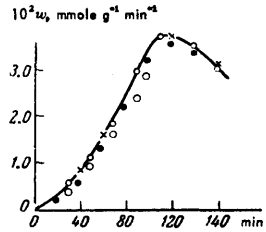


Fig. 5. Comparison of curves for the rate of formation of oxidation products of polypropylene with the rate curve for the formation of water, made by plotting the rates on different scales: ○) acetone; ●) acetaldehyde; ×) hydrogen peroxide.

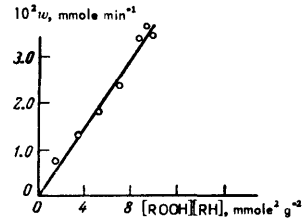


Fig. 6. Dependence of rate of formation of oxidation products of polypropylene on peroxide concentration.

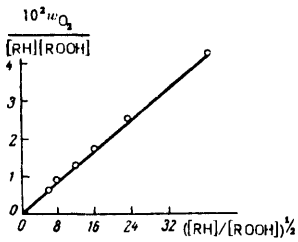


Fig. 3. Dependence of rate of absorption of oxygen on the concentrations [RH] and [ROOH].

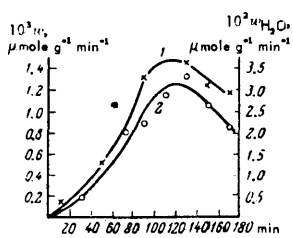


Fig. 4. Variation, during the oxidation of polypropylene at 130° and p_{O_2} = 400 mm, in rate of formation of: 1) water; 2) acetone.

above concentration product also shows that the hydroperoxide breaks down as a result of reaction with the polymer, according to the equation

$$ROOH + RH \longrightarrow RO^{\cdot} + H_2O + R^{\cdot},$$

i.e. by a bimolecular mechanism, not by a unimolecular mechanism as suggested above.

The possibility of such a mechanism for the decomposition of peroxides had been mentioned earlier[51-53], as the heat absorbed in this reaction (15 kcal mole^{-1}) was less by 25 kcal mole^{-1} than the quantity absorbed in the unimolecular decomposition. Breakdown of a hydroperoxide would be still more rapid if it reacted with a compound in which the bond energy of the hydrogen atom were less than in RH.

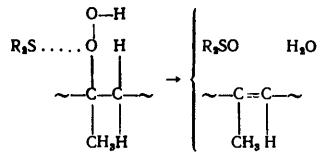
The energy of the N–H bond in antioxidants is considerably lower than that of the C–H bond in hydrocarbons. Rates of decomposition of the hydroperoxide formed in the oxidation of isotactic polypropylene have been compared[54,55] in the absence and in the presence of antioxidants. The rate of decomposition of the hydroperoxide in the presence of polypropylene at temperatures between 90° and 130° was found to be considerably lower than the rate of breakdown

of the same hydroperoxide when *N*-cyclohexyl-*N'*-phenyl-*p*-phenylenediamine (0.38 mmole g^{-1}) was added to the polypropylene (Fig. 7).

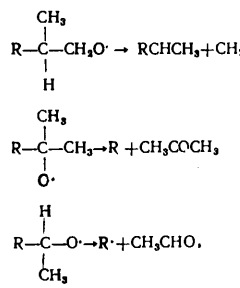
The activation energy of the decomposition of polypropylene hydroperoxide in polypropylene was found to be 25 kcal $mole^{-1}$, and in the presence of the above antioxidant 13 kcal $mole^{-1}$.

Ingold has recently shown that several antioxidants belonging to the substituted phenol and aromatic amine class also accelerate the breakdown of the hydroperoxides formed in the oxidation of a white mineral oil[56].

Dialkyl sulphides accelerate the decomposition of polypropylene hydroperoxide by a different mechanism. Data on the effect of added dihexadecyl sulphide on the decomposition[55] at 110° show (Fig. 8) that the hydroperoxide concentration falls extremely slowly in the absence of the sulphide, but considerably more rapidly at the start of the reaction in its presence. The rate of formation of water during decomposition of the hydroperoxide in the presence of the sulphide is characterised by a well-defined maximum. Such reaction kinetics can be explained by the formation of an addition product between the sulphide and the hydroperoxide, which breaks down into a sulphoxide, water, and an olefin as follows:

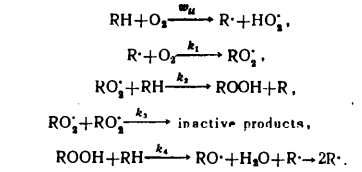


The bimolecular decomposition of hydroperoxides always involves the formation of water, alkyl radicals, and alkoxy-radicals. Breakdown of the latter radicals can yield, depending on their structure, formaldehyde, acetone, acetaldehyde, and other volatile products:



as well as non-volatile alcohols, ketones, and aldehydes, the presence of which in the oxidised polymer is shown by the infrared spectra. The non-volatile products contain about 70% of absorbed oxygen.

The observed facts are well explained by the following scheme for the oxidation of polypropylene:



From this scheme we derive the following differential equations representing the variation in concentration of the radicals R$^{\bullet}$ and $RO_2^{\bullet}$

$$\frac{d[R^{\bullet}]}{dt} = w_u + k_2[RH][RO_2^{\bullet}] + 2k_4[RH][ROOH] - k_1[R^{\bullet}][O_2]. \quad (1)$$

$$\frac{d[RO_2^{\bullet}]}{dt} = k_1[R^{\bullet}][O_2] - k_2[RH][RO_2^{\bullet}] - k_3[RO_2^{\bullet}]^2. \quad (2)$$

Applying the Bodenstein–Semenov method and combining these equations, we obtain

$$w_u + 2k_4[RH][ROOH] - k_3[RO_2^{\bullet}]^2 = 0. \quad (3)$$

Hence for the concentration of $RO_2^{\bullet}$ radicals we find the expression

$$[RO_2^{\bullet}] = \sqrt{\{w_u + 2k_4[RH][ROOH]\}/k_3}. \quad (4)$$

Bearing in mind that $k_1[R^{\bullet}][O_2]$ is equal to the rate of absorption of oxygen w_{O_2}, substituting for $[RO_2^{\bullet}]$ in Eqn. (1), and neglecting w_u, we obtain

$$w_{O_2} = k_2\sqrt{2k_4/k_3}\,[RH]^{1/2}[ROOH]^{1/2} + 2k_4[RH][ROOH]. \quad (5)$$

Division of both sides of Eqn. (5) by [RH][ROOH] converts it into

$$\frac{w_{O_2}}{[RH][ROOH]} = 2k_4 + k_2\sqrt{\frac{2k_4}{k_3}\,\frac{[RH]}{[ROOH]}}. \quad (6)$$

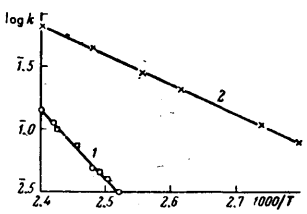


Fig. 7. Temperature dependence of rate of decomposition of polypropylene hydroperoxide: 1) in the presence of *N*-cyclohexyl-*N'*-phenyl-*p*-phenylenediamine; 2) in the absence of this antioxidant; □) results obtained by iodometric titration; ×) results obtained from the rate of formation of the products.

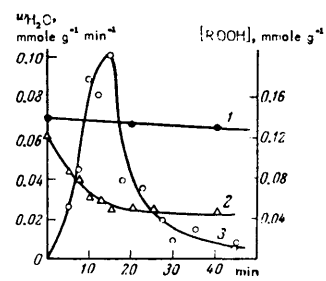


Fig. 8. Kinetics of the decomposition of polypropylene hydroperoxide at 110°: 1) alone; 2) in the presence of dihexadecyl sulphide (0.29 mmole g^{-1}); 3) rate of formation of water in the presence of the sulphide (left-hand scale).

If the above mechanism corresponds to the oxidation of polypropylene, the dependence of rate of absorption of oxygen on hydroperoxide concentration should give a linear relation between

$$\frac{w_{O_2}}{[RH]\,[ROOH]} \text{ and } \sqrt{\frac{[RH]}{[ROOH]}}.$$

Fig. 6 shows that the experimental results agree well with Eqn. (6).

If water and other volatile products are formed by the breakdown of hydroperoxides, the rates of formation w of volatile products in the thermal decomposition of hydroperoxides should decrease with time in proportion to the diminution in the concentration of peroxides. Experimental results for the rates of formation of water, acetone, and aldehydes can be made to fit well on a single curve by appropriate choice of scale (Fig. 9), the equation of this curve representing the variation in concentration of the hydroperoxide undergoing decomposition. In Fig. 9 the scales on which rates of formation of water, acetone, formaldehyde, and acetaldehyde are plotted are in the ratios 1 : 40 : 72 : 138.

It is significant that the relative rates of formation of volatile products in the oxidation of polypropylene and in the decomposition of hydroperoxides are practically the same (see Table).

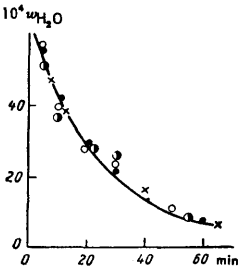


Fig. 9. Variation in rates w of formation of volatile products in the decomposition of polypropylene hydroperoxide at 130°: ○) acetone; ◑) water; ×) acetaldehyde; ●) formaldehyde.

TABLE. Relative rates of formation of volatile products in the oxidation of polypropylene and in the decomposition of hydroperoxides.

Product	Oxidation of polypropylene	Decomposition of hydroperoxides
H_2O	1	1
CH_3COCH_3	0.025	0.025
CH_2O	0.017	0.014
CH_3CHO	0.008	0.007

The results cited above show that hydroperoxides constitute the primary oxidation product of polypropylene, and their decomposition yields several volatile and non-volatile secondary products.

4. CRITICAL ANTIOXIDANT CONCENTRATION

About forty years ago Christiansen[57] and Bäckstrom[58] explained the inhibition of oxidation by small amounts of impurities on the assumption that oxidation is a chain process and that the impurities terminate the reaction chains. This theory was developed by Semenov[5].

It is generally accepted that carbon-chain polymers are oxidised by a chain mechanism involving degenerate branching[3]. Initiation results from the attack of oxygen on the RH molecule according to the equation

$$RH+O_2 \xrightarrow{w_u} R^{\cdot}+HO_2^{\cdot}.$$

The chain reaction is propagated *via* the radicals R$^{\cdot}$ and $RO_2^{\cdot}$:

$$ROO^{\cdot}+RH \xrightarrow{k_2} ROOH+R^{\cdot},$$

$$R^{\cdot}+O_2 \xrightarrow{k_3} RO_2^{\cdot},$$

hydroperoxide molecules being formed as the primary reaction product, which can then decompose, giving rise to branching:

$$ROOH \xrightarrow{k_4} RO^{\cdot}+H\dot{O}.$$

It is assumed that antioxidants JH react with active $RO_2^{\cdot}$ radicals to form inactive products:

$$RO_2^{\cdot}+JH \xrightarrow{k_5} \text{inactive products}.$$

Semenov showed that a consequence of the above mechanism, described by the differential equations

$$\frac{d[RO_2^{\cdot}]}{dt} = w_u - k_5[JH][RO_2^{\cdot}] + k_4[ROOH], \quad (7)$$

$$\frac{d[ROOH]}{dt} = k_2[RH]\,[RO_2^{\cdot}] - k_4[ROOH], \quad (8)$$

is the presence of a "critical" antioxidant concentration[6]. In fact, a solution of these linear equations can be written

$$[RO_2^{\cdot}] = \Sigma A_i e^{\lambda_i t} + B_i, \quad (9)$$

where the λ_i are the roots of the secular determinant

$$\begin{vmatrix} -k_5[JH]-\lambda & k_4 \\ k_2[RH] & -k_4-\lambda \end{vmatrix} = 0. \quad (10)$$

This yields the quadratic equation

$$\lambda^2 + \{k_4 + k_5[JH]\}\lambda + k_4k_5[JH] - k_2k_3[RH] = 0. \quad (11)$$

Since the coefficient of λ is positive, the sum of the roots of the equation is negative. This means either that both roots are negative or that one root is positive while the other is negative but larger in absolute magnitude. If both roots are negative, the values of $[RO_2^{\cdot}]$ and [ROOH] do not increase to infinity but tend to a constant value: *i.e.* we are dealing with a stationary slow reaction. If one root is positive, the radical concentration increases all the time, and we are dealing with a non-stationary accelerating process.

Whether a process is stationary or non-stationary can be determined by finding the sign of the independent term in Eqn. (11). If

$$[JH] > \frac{k_2}{k_5}[RH], \quad (12)$$

the independent term is positive, and hence both roots of Eqn. (11) are negative. Thus if the inequality (12) is observed, the oxidation process is stationary, and consequently the antioxidant is preventing acceleration of the oxidation. If

$$[JH] < \frac{k_3}{k_4}[RH], \qquad (13)$$

the independent term in Eqn. (11) is negative, and hence one root of this equation is positive. Hence the radical concentration will increase to high values in conformity with Eqn. (9), and oxidation will be accelerated, *i.e.* will be non-stationary.

The antioxidant concentration defined by the equation

$$[JH]_{cr} = \frac{k_3}{k_5}[RH], \qquad (14)$$

is termed the "critical" concentration. At lower antioxidant concentrations the oxidation is a non-stationary process, and at higher concentrations it is stationary.

A similar result has been obtained by a somewhat different method[59]. If the number of radicals is n, the rate of initiation w_u, the autocatalytic factor φ, and the concentration of antioxidant x,

$$\frac{dn}{dt} = w_u + \varphi n - knx, \qquad (15)$$

$$-\frac{dx}{dt} = knx, \qquad (16)$$

where k is the velocity constant for reaction of the radicals with the antioxidant. Clearly, when

$$kx < \varphi, \qquad (17)$$

the reaction will be autocatalytic; but when

$$kx > \varphi, \qquad (18)$$

it will be a stationary reaction. Thus the critical antioxidant concentration is given by the equation

$$x_{cr} = \varphi/k. \qquad (19)$$

If condition (18) holds at the start of the reaction, the radical concentration will soon reach a stationary value, which will be maintained for a period of time between 0 and τ, during which the concentration x will fall comparatively slowly to the value x_{cr}, as shown in Fig. 10. The reaction will then begin to accelerate, with the radical concentration increasing rapidly, while the antioxidant concentration will drop rapidly to zero.

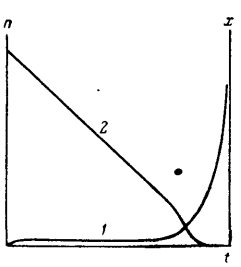


Fig. 10. Variation in concentration during a chain oxidation: 1) radicals n; 2) antioxidant x.

Several workers have shown[47,59-62] that a critical concentration is in fact observed in the inhibition of the oxidation of liquid hydrocarbons and polymers by various antioxidants (Fig. 11).

In the book by Emanuel' and Lyaskovskaya[63] the mechanism of the inhibition of oxidation is corrected by replacing the equation

$$RO_3^{\cdot} + JH \rightarrow \text{inactive products},$$

with

$$RO_3^{\cdot} + JH \rightarrow ROOH + J^{\cdot}.$$

However, the whole of Semenov's derivation is repeated unchanged, the secular equation (10) and the formula for the critical inhibitor concentration (14) being given without change. Nevertheless, if the reasonable correction of Emanuel' is accepted, Eqn. (8) must be replaced by

$$\frac{d[ROOH]}{dt} = k_3[RH][RO_3^{\cdot}] + k_5[JH][RO_3^{\cdot}] - k_4[ROOH], \qquad (20)$$

when the secular equation will become

$$\begin{vmatrix} k_5[JH] - \lambda & k_1 \\ k_3[RH] + k_5[JH] & -k_2 - \lambda \end{vmatrix} = 0. \qquad (21)$$

Under these conditions the independent term in the quadratic equation for λ will be independent of [JH] and always negative. This means that one root of the quadratic equation will be positive, and the oxidation will be non-stationary at all antioxidant concentrations. Thus the scheme which has been adopted provides no explanation of the occurrence of a critical antioxidant concentration.

The generally accepted mechanism of the inhibition of oxidation is based on the following hypotheses: (1) the inhibitor terminates reaction chains, but does not affect the initiation of chains; (2) the hydroperoxide decomposes with formation of two active radicals. It follows from these postulates that the inhibitor is consumed according to a linear law if its concentration exceeds a critical value. The rate of consumption of the inhibitor is then equal to the rate of initiation, and the induction period increases in proportion to the inhibitor concentration.

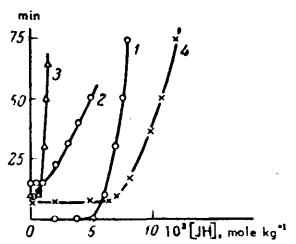


Fig. 11. Dependence of induction period in oxidation on antioxidant concentration: 1) poly(ethylene oxide) and Stabiliser 22-46 at 145° and (p_{O_2}) 340 mm; 2) tetralin and tri-t-butylphenol at 140° and 300 mm; 3) pentane and diphenylamine at 170° and 300 mm; 4) polypropylene and phenyl-2-naphthylamine at 200° and 300 mm.

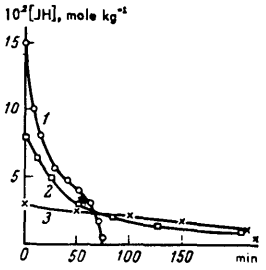


Fig. 12. Consumption of antioxidants in polypropylene at 200° and p_{O_2} = 300 mm: 1) 2,6-bis-(1,1-dimethylhexyl)-4-methylphenol; 2) methylenebis-2,2′-(4-methyl-6-t-butylphenol); 3) phenyl-1-naphthylamine.

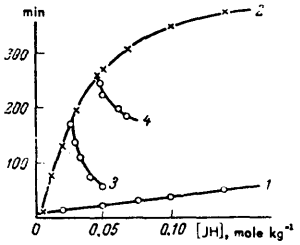


Fig. 13. Induction period in the oxidation of polypropylene at 200° and p_{O_2} = = 300 mm in the presence of antioxidants: 1) 2,6-bis-(1,1-dimethylhexyl)-4-methylphenol; 2) methylenebis-2,2′-(4-methyl-6-t-butylphenol); 3) and 4) mixtures of these two antioxidants.

Experimental work has shown that the above assumptions are not in fact justified. Antioxidants are not usually consumed according to a linear law[64]. Thus 2,6-bis-(1,1-dimethylhexyl)-4-methylphenol, on addition to polypropylene, at first disappears rapidly, then more slowly, and after that again more rapidly. The antioxidant methylenebis-2,2′-(4-methyl-6-t-butylphenol) in polypropylene is used up according to a first-order law until its concentration falls to a critical value, after which it vanishes rapidly. If polypropylene is stabilised with phenyl-1-naphthylamine, the latter is consumed during oxidation, at first slowly and then considerably more rapidly. Curves representing the consumption of these antioxidants are illustrated in Fig. 12. Similar results have been obtained by Likhtenshtein[65], who has investigated the kinetics of the consumption of diphenylamine in the inhibition of the oxidation of polypropylene, hexadecane, and other hydrocarbons.

5. INITIATION OF OXIDATION BY ANTIOXIDANTS

The above results indicate the complexity of the action of antioxidants. It may be thought that they not only terminate reaction chains but also are able to initiate oxidation. If an antioxidant only terminates chains, its introduction into a polymer cannot shorten the induction period, but this can occur under certain conditions if it is able also to initiate chains.

In order to realise such conditions, methylenebis-2,2′-(4-methyl-6-t-butylphenol) was added (0.02 mole kg^{-1}) to polypropylene, when the induction period at 200° and an oxygen pressure of 300 mm was increased to 180 min. If another antioxidant, 2,6-bis-(1,1-dimethylhexyl)-4-methylphenol, was added to the polypropylene stabilised in this way, the induction period fell from 180 to 50 min[64], as shown in Fig. 13. Ingold observed a similar effect, which he termed "antagonistic", on the addition to a hydrocarbon fuel of two antioxidants, 2,4,6-trimethylphenol and *N*-phenyl-1-naphthylamine, or methylenebis-2,2′-(4-methyl-6-t-butylphenol) and *NN′*-di-s-butyl-*p*-phenylenediamine[56]. An antagonistic effect of this kind was observed in the inhibition of polypropylene oxidation by several antioxidant mixtures.

The ability of antioxidants to initiate oxidation also provides an explanation of the fact that, with increase in the inhibitor concentration, the induction period increases more slowly than linearly, as shown by the typical curve in Fig. 14.

The efficiency of an antioxidant will clearly depend on the relative rates of chain termination and initiation. Since the latter process is characterised by the higher activation energy, a rise in temperature produces a more rapid increase in the rate of initiation than in the rate of chain termination. Therefore the efficiency of an antioxidant should diminish with rise in temperature, as is actually observed experimentally.

Initiation by antioxidants has not yet been subjected to detailed investigation, but three probable mechanisms can be suggested for this process. Firstly, initiation may result from oxidation of the inhibitor by the reaction

$$JH + O_2 \rightarrow HO_2^{\cdot} + J\,.$$

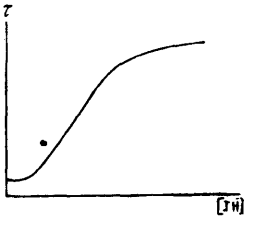


Fig. 14. Typical curve for variation of induction period with antioxidant concentration.

with formation of the comparatively active radical $HO_2^\cdot$, whose presence during oxidation has recently been proved by the EPR method[13]. Secondly, relatively inactive inhibitor radicals J$^\cdot$ can sometimes react with polymer molecules:

$$J^\cdot + RH \rightarrow JH + R^\cdot,$$

active radicals being formed. The possibility of such a reaction has been demonstrated by the EPR method[66]. Finally, antioxidants may initiate oxidation by reacting with hydroperoxides[55,67]:

$$ROOH + JH = RO^\cdot + H_2O + J^\cdot.$$

A significant fact indicating initiation of a reaction which consumes the antioxidant is the fall in molecular weight of the polymer during the induction period, when the number of ruptured bonds is proportional to such consumption[68].

This phenomenon is seen especially well in the oxidative thermal degradation of polypropylene to which has been added di-t-butylcresyl disulphide†, investigated by Lukovnikov *et al.*[69] Fig. 15 shows that the induction period is greatly increased, but the molecular weight of the polymer drops rapidly.

Thus the assembly of known facts leads to the conclusion that the first assumption, that antioxidants do not influence initiation, is incorrect. The second assumption, that two active radicals are formed on the breakdown of a hydroperoxide, is probably also of doubtful validity. Several papers have shown[70,71] that hydroperoxides can decompose in solution without forming radicals and without initiating chains.

The conditions under which a "critical" antioxidant concentration is possible can be determined, as Shlyapnikov has shown[72], if the hypothesis, that breakdown of a hydroperoxide ultimately yields δ active $RO_2^\cdot$ radicals, is introduced into the scheme of polymer oxidation.

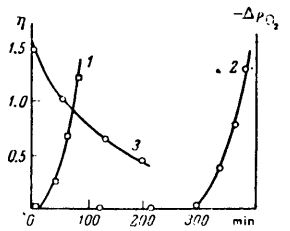


Fig. 15. Oxidation of polypropylene: 1) absorption of oxygen by unstabilised polymer; 2) absorption of oxygen by polymer stabilised with di-t-butyl-*p*-cresyl disulphide† and catechol naphthol phosphite; 3) fall in viscosity in latter case.

† The Russian nomenclature is obscure: perhaps di-(2-hydroxy-5-methyl-3-t-butyl) disulphide is meant (Ed. of Translation).

The mechanism of the oxidation of a polymer RH containing an antioxidant JH can be represented by the following scheme:

$$JH + O_2 \xrightarrow{w_u} J^\cdot + HO_2^\cdot \rightarrow RO_2^\cdot,$$
$$RO_2^\cdot + RH \xrightarrow{k_2} ROOH + R^\cdot,$$
$$ROOH + RH \xrightarrow{k_4} \delta RO_2^\cdot,$$
$$RO_2^\cdot + JH \xrightarrow{k_5} ROOH + J^\cdot.$$

If a sulphide R_2S, capable of breaking down the hydroperoxide without forming active products[73], is added to the polymer, the equation

$$ROOH + R_2S \xrightarrow{k_6} \text{inactive products},$$

must be added to the above scheme. In this case Eqns. (7) and (8) become

$$\frac{d[ROOH]}{dt} = k_2[RH][RO_2^\cdot] + k_5[JH][RO_2^\cdot] - k_4[RH][ROOH] - k_6[R_2S][ROOH]. \quad (22)$$

$$\frac{d[RO_2^\cdot]}{dt} = w_u - k_5[JH][RO_2^\cdot] + k_4[RH][ROOH]. \quad (23)$$

The secular determinant may be written

$$\begin{vmatrix} -k_4[RH] - k_6[R_2S] - \lambda & k_2[RH] + k_5[JH] \\ k_4[RH] & -k_5[JH] - \lambda \end{vmatrix} = 0, \quad (24)$$

or in expanded form

$$\lambda^2 + \{k_4[RH] + k_5[JH] + k_6[R_2S]\}\lambda + k_4k_5[RH][JH] + k_5k_6[JH][R_2S] - k_2k_4[RH]^2 - k_4k_5[RH][JH] = 0. \quad (25)$$

An analysis similar to that of Eqn. (11) enables us to calculate the critical antioxidant concentration as

$$[JH]_{cr} = \frac{\delta k_2 k_4 [RH]^2}{(1-\delta)k_4k_5[RH] + k_5k_6[R_2S]}. \quad (26)$$

In the particular case in which the concentration $[R_2S]$ is zero, we obtain

$$[JH]_{cr} = \frac{\delta}{1-\delta} \times \frac{k_2}{k_5} \times [RH]. \quad (27)$$

From Eqn. (27) it is evident that a stationary reaction and a critical antioxidant concentration can occur only if $\delta < 1$, *i.e.* when decomposition of the hydroperoxide yields on the average less than one active radical. If $\delta \geq 1$, the reaction is non-stationary at all antioxidant concentrations, and no critical concentration of antioxidant exists.

6. THEORY OF SYNERGISM

Even if $\delta > 1$, addition to the polymer of the sulphide R_2S in sufficient concentration may make the denominator on the right-hand side of Eqn. (26) positive, which will allow a critical antioxidant concentration to be realised. The correctness of this conclusion has been confirmed experimentally[72].

When the antioxidant 2,6-bis-(1,1-dimethylhexyl)-4-methylphenol is added in various concentrations to polypropylene, the induction period at 200° and p_{O_2} = 300 mm increases linearly from 8 min to 65 min: *i.e.* no critical concentration of the antioxidant is observed. If didecyl sulphide is added as well as the above phenol, a critical concentration is clearly evident, which in conformity with Eqn. (26) diminishes with increasing concentration of the sulphide (Fig. 16).

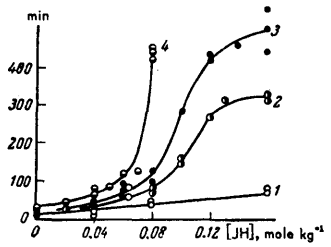


Fig. 16. Dependence of induction period in the oxidation of polypropylene on concentration of 2,6-bis-(1,1-dimethylhexyl)-4-methylphenol at 200° and p_{O_2} = 300 mm in the presence of different concentration (mole kg^{-1}) of didecyl sulphide: 1) 0; 2) 0.04; 3) 0.08; 4) 0.12.

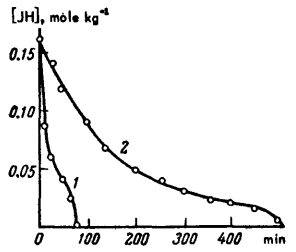


Fig. 18. Consumption of 2,6-bis-(1,1-dimethylhexyl)-4-methylphenol in the oxidation of polypropylene at 200° and p_{O_2} = 300 mm: 1) alone; 2) in the presence of didecyl sulphide.

Didecyl sulphide itself is an inefficient antioxidant, its addition to polypropylene lengthening the induction period only very slightly. However, addition to the polymer of 2,6-bis-(1,1-dimethylhexyl)-4-methylphenol as well as the sulphide produces a sharp increase in the induction period with the appearance of a critical concentration (Fig. 17).

Addition of didecyl sulphide to polypropylene greatly diminishes the rate of consumption of 2,6-bis-(1,1-dimethylhexyl)-4-methylphenol (Fig. 18). Similarly, but to a smaller extent, the rate of consumption of the antioxidant methylenebis-2,2'-(4-methyl-6-t-butylphenol) in polypropylene is decreased by the addition of didecyl sulphide, as is evident from the curves in Fig. 19. These facts are fully consistent with the theory developed in Ref. 72.

The mutual strengthening of effectiveness observed in mixtures of 2,6-bis-(1,1-dimethylhexyl)-4-methylphenol and didecyl sulphide is due to breakdown of the hydroperoxide and the slowing down in the consumption of antioxidant. Either of these oxidation inhibitors alone lengthens the induction period only slightly. When mixed, however, they are able to extend the induction period in the oxidation of polypropylene to 450 min at 200° and p_{O_2} = 300 mm, as shown in Fig. 20.

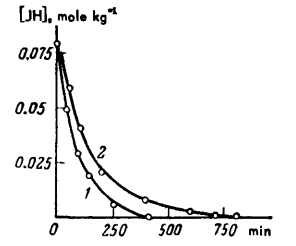


Fig. 19. Consumption of methylenebis-2,2'-(4-methyl-6-t-butylphenol) in the oxidation of polypropylene at 200° and p_{O_2} = 300 mm: 1) alone; 2) in the presence of didecyl sulphide.

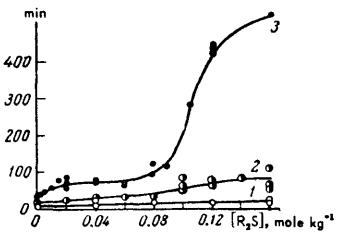


Fig. 17. Dependence of induction period on concentration of didecyl sulphide at 200° and p_{O_2} = 300 mm in the presence of different concentrations (mole kg^{-1}) of 2,6-bis-(1,1-dimethylhexyl)-4-methylphenol: 1) 0; 2) 0.04; 3) 0.08.

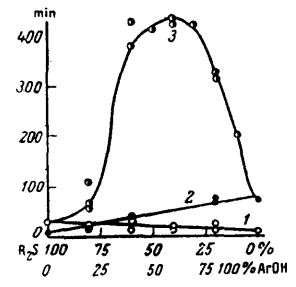


Fig. 20. Dependence of induction period in oxidation of propylene at 200° and p_{O_2} = = 300 mm on: 1) concentration of didecyl sulphide; 2) concentration of 2,6-bis-(1,1-dimethylhexyl)-4-methylphenol; 3) mole fractions of these stabilisers when their total concentration is 0.2 mole kg^{-1}.

There can be no doubt that many cases of the mutual strengthening of effectiveness observed when mixtures of antioxidants and sulphides are added to polymers [66,74] are explained by the above theory. The most efficient of the mixtures investigated to date contains catechol 4-methyl--2,6-di-t-butylphenol phosphite and bis-2-hydroxy-4-t--butyl-*m*-tolyl sulphide (SAO-6). At a total concentration of 0.015 mole kg^{-1} this mixture lengthens the induction period in the oxidation of polypropylene at 200° and p_{O_2} = = 200 mm to 400 min (Fig. 21).

When an antioxidant radical J· causes the initiation of oxidation, the effectiveness of the antioxidant can be increased by adding a second substance which captures the J· radicals. Likhtenshtein has shown [75] that such a case occurs in the stabilisation of polypropylene with diphenylamine if polyphenylene or diphenylpicrylhydrazyl is added to the polymer as a second substance.

Fig. 22 illustrates the results obtained in this paper. With increase in the diphenylamine concentration the induction period τ slowly increases (curve *1*). If both diphenylamine and polyphenylene are added to the polypropylene, the variation of τ with the diphenylamine concentration (curve *2*) shows a well developed mutual strengthening effect, and the appearance of a critical antioxidant concentration is clearly evident.

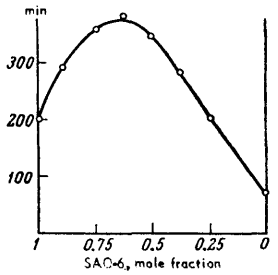


Fig. 21. Induction period in the oxidative thermal degradation, at 200° and p_{O_2} = = 200 mm, of polypropylene, stabilised with mixtures of SAO-6 and the phosphite of catechol and 4-methyl-2,6-di-t-butylphenol (total stabiliser concentration 0.015 mole kg^{-1}).

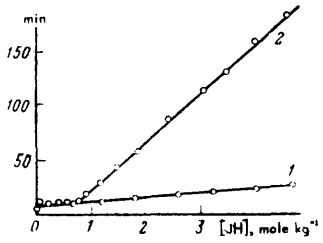


Fig. 22. Dependence of induction period, in the oxidative thermal degradation of stabilised polypropylene at 172° and p_{O_2} = = 200 mm, on the concentration of diphenylamine: 1) in the absence of polyphenylene; 2) in the presence of 3% of polyphenylene.

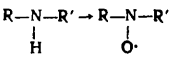
The phenomenon of the mutual strengthening of the action of antioxidants, often termed "synergism", has been discussed in detail in several monographs and reviews [63,67,76,77].

The results discussed above clearly show how disadvantageous is the fact that antioxidants are involved in the initiation of oxidation as well as the termination of chains. The most important part here is played by the formation of hydroperoxides in the reaction of peroxide radicals $RO_2^{\cdot}$ with antioxidants containing loosely combined hydrogen. Among such antioxidants are the widely employed derivatives of phenols and aromatic amines.

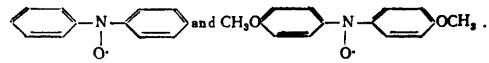
It seems to the Reviewer that one of the most important problems in the inhibition of oxidation is the search for new classes of antioxidants, not containing weakly bound hydrogen. In this respect, triesters of phosphorus acid [78] and also polyphenylenes, polyphenylacetylenes, and polyazophenylenes [79] are undoubtedly of interest.

7. FREE RADICALS AS STABILISERS

In connection with the above problem, an attempt has been made to use as antioxidants, instead of amine derivatives, radicals obtained by replacing the active amino--hydrogen by an oxygen atom:



The following radicals have been synthesised [80]:

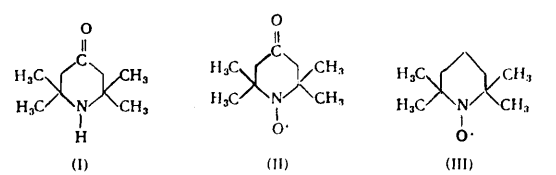


These comparatively stable radicals are good antioxidants for polypropylene and several liquid hydrocarbons.

The fact that the nitric oxide radical obtained by oxidising diphenylamine is itself an antioxidant was noted by Thomas, who compared the inhibition of the oxidation of white mineral oil by small additions of diphenylamine and of diphenyl nitric oxide [81].

Likhtenshtein's experiments have shown [65] that diphenyl nitric oxide is consumed very slowly during the induction period in the oxidation of hexadecane at 150°, probably at the same rate as initiation. The rate of consumption of diphenyl nitric oxide does not increase until the end of the induction period (Fig. 23).

Aliphatic nitric oxides have also been synthesised [82] from 2,2,6,6-tetramethyl-4-oxopiperidine (I), their formulae being given below



(I) (II) (III)

The radical (II) is a far better antioxidant for polypropylene [62] than is (I), as can be seen from Fig. 24. This is probably

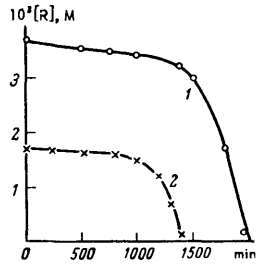


Fig. 23. Consumption of diphenylnitric oxide in the oxidation of hexadecane at 150° and p_{O_2} = 500 mm with different initial concentrations of the radical: 1) 0.0038 M; 2) 0.0018 M.

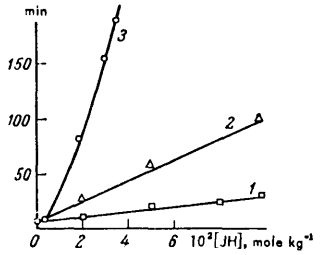
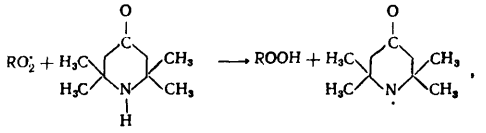
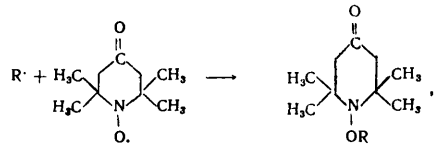


Fig. 24. Dependence of induction period in oxidation of polypropylene at 170° on concentration of: 1) 2,2,6,6-tetramethyl-4-oxopiperidine (I); 2) diphenylamine; 3) nitric oxide radical (II) of (I).

associated with the fact that the latter reacts with $RO_2^{\cdot}$ radicals as follows:



whereas (II) adds on R· radicals according to the equation



without the formation of peroxide molecules.

The great stability of the radicals (II) and (III) is probably due to effective screening of the NO by the methyl groups.

The radical (II) is a good antioxidant, inhibiting the oxidative thermal degradation of polyamides. Whereas capron [brand of 6-polyamide fibre produced in the Soviet Union (Ed. of Translation)] absorbs oxygen at 180° without an appreciable induction period, whether it is unstabilised or has been stabilised with the usual antioxidants, addition of small amounts of the radical (II) delays by many minutes the start of appreciable absorption of oxygen.

The consumption of the radical (II) during the induction period has been measured by the EPR method. It is only after the EPR signal has vanished, *i.e.* after all the radical has been used up, that autocatalytic oxidation of the capron begins, as can be seen from the curves in Fig. 25.

The induction period in the oxidation of capron at 200° and an oxygen pressure of 200 mm becomes longer with increase in the concentration of radical (II) (Fig. 26). A critical antioxidant concentration is observed in this case, probably indicating the occurrence of a stationary reaction which is the result of chain termination without simultaneous formation of hydroperoxides and initiation of oxidation. All known stabilisers for capron diminish the rate of absorption of oxygen, as is observed when the radical (II) is employed as antioxidant.

Since the radical (II) has demonstrated its universality as antioxidant in the oxidation of several hydrocarbons, polypropylene, and polyamides, it has been tried as an inhibitor of the oxidative thermal degradation of polyformaldehyde, which is rapid[83,84] at 200°. Enikolopyan[85] has shown that degradation of polyformaldehyde begins at the

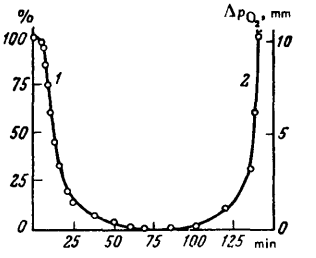


Fig. 25. Induction period in the oxidation of 6,8-polyamide: 1) consumption of (II); 2) absorption of oxygen (right-hand scale).

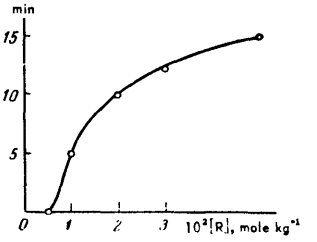


Fig. 26. Dependence of induction period in oxidation of 6,8-polyamide at 200° and p_{O_2} = = 200 mm on concentration of (II).

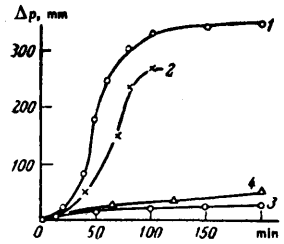


Fig. 27. Increase in pressure accompanying the oxidation of acetylated polyformaldehyde at 200° and p_{O_2} = 600 mm: 1) alone; 2) in the presence of 2% of polyamide; 3) in the presence of 1.2% of polyamide + 0.8% of (II); 4) oxidation of Delrin.

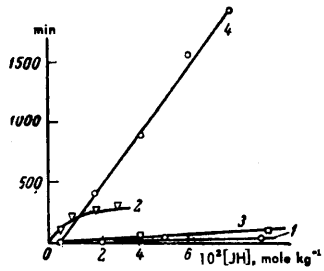


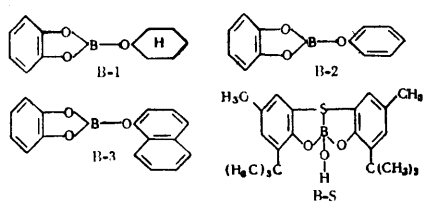
Fig. 28. Dependence of induction period in the oxidation of polypropylene at 200° and p_{O_2} = 300 mm on concentration of: 1) 2,6-bis-(1,1-dimethylhexyl)-4-methylphenol; 2) Stabiliser 22-46; 3) Polygard; 4) ester of SAO-6 and boric acid.

ends of the molecule, with the liberation of formaldehyde, which reacts with oxygen to give formic acid. In order to stabilise polyformaldehyde, a polyamide must be added to it to combine with the formaldehyde, and also a substance to bind the formic acid. Addition to an acetylated polyformaldehyde of 1.2% of a polyamide resin and 0.8% of radical (II) provides excellent stabilisation, the resulting product being more stable than Delrin (see Fig. 27). It can be supposed that some radicals are formed by the oxidative thermal degradation of polyformaldehyde, and these are captured by the radical (II).

Work on radical inhibitors has started only recently, and the progress achieved in a short time suggests that it is a promising line of research.

8. BORATE STABILISERS

Another line of work in the search for new stabilisers for polymers is the use as antioxidants of orthoboric esters containing no weakly bound hydrogen. Several such esters have been described[86], and the structural formulae of some of the most effective antioxidants among the esters which have been tested are given below:



The antioxidants B-1, B-2, and B-3 are esters formed by catecholboric acid with cyclohexanol, phenol, and 1-naphthol respectively. They are all good antioxidants, inhibiting the oxidative thermal degradation of polypropylene at 200°. B-2 and B-3 have well marked critical concentrations. B-3 is a strong antioxidant, while B-2 and B-1 are considerably weaker.

It is interesting that the ester of boric acid and the bis-hydroxyphenyl sulphide SAO-6, which has been labelled B-S above, has proved the most effective antioxidant among all the boric esters which we have investigated, in spite of the presence of a hydroxy-hydrogen in its molecule.

Fig. 28 illustrates experimental induction periods for the oxidation of polypropylene, stabilised with various antioxidants, at 200° and p_{O_2} = 200 mm. It is evident that B-S is a far more efficient stabiliser than 2,6-bis(1,1-dimethylhexyl)-4-methylphenol, Stabiliser 22-46, or Polygard. At a concentration of 0.04 mole kg^{-1} it inhibits oxidation for 840 min, whereas Polygard delays oxidation by only 50 min, and Stabiliser 22-46 by about 300 min.

It can be hoped that the search for new antioxidants may be the starting point for the development of research in this important field for polymer chemistry.

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1,3-DICHLOROBUT-2-ENE AND NEW PREPARATIONS BASED ON IT

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I. INTRODUCTION

Soon after its discovery, 1,3-dichlorobut-2-ene, one of the side-products of the manufacture of chloroprene rubber [1-5], attracted the attention of chemists who attempted to find applications for it. There are several reviews dealing with the reactions of 1,3-dichlorobut-2-ene and its applications [6-9], the last (published in 1954) covering only certain aspects of this problem. Since in recent years many papers have appeared, describing various interesting syntheses based on this compound, we have attempted an assessment of the importance of the investigations which have been made.

In the manufacture of chloroprene rubber 1,3-dichlorobut-2-ene is formed as a result of the addition of a second molecule of hydrogen chloride to vinylacetylene in the presence of a copper catalyst [1,2]:

$$HC\equiv C-CH=CH_2 \xrightarrow[CuCl]{HCl} [CH_2=C=CH-CH_2Cl] \rightarrow$$
$$\rightarrow CH_2=CCl-CH=CH_2 \xrightarrow[CuCl]{HCl} CH_3CCl=CH-CH_2Cl.$$

Under the usual conditions of chloroprene synthesis the yield of 1,3-dichlorobut-2-ene does not exceed 3%, but it can clearly be increased by using an excess of hydrochloric acid [2]. Carothers, who first described 1,3-dichlorobut-2-ene, quotes the following physical constants for this compound: b.p. 127-129°/756 mm and 53-54°/50 mm; d_4^{20} 1.1591; n_D^{20} 1.4724. [2] Distilled 1,3-dichlorobut-2-ene is a colourless liquid with a sharp smell and lachrymatory action.

Later it was found that the 1,3-dichlorobut-2-ene obtained by dehydrochlorination of monovinylacetylene consists of two stereosiomers (*cis* and *trans*). Hatch and coworkers separated the geometrical isomers of 1,3-dichlorobut-2-ene by fractional distillation and investigated their properties [10-13]. According to their data, the mobility of the allyl chlorine in the high-boiling β-isomer (b.p. 131°/748 mm) is higher than in the low-boiling α-isomer (b.p. 127.8°/745 mm), while the latter is higher than in allyl chloride [11-13]. Heating favours the conversion of the β-isomer to the α-isomer [10,11].

The configuration of the stereoisomers was convincingly demonstrated by reduction of the α and β forms with $LiAlH_4$ to the *trans*- and *cis*-2-chlorobut-2-enes respectively [13]:

$$ClCH_2-\underset{\|}{C}(Cl)-CH_3 \rightarrow CH_3-\underset{\|}{C}(Cl)-CH_3 \qquad H-\underset{\|}{C}(Cl)-CH_2Cl \rightarrow H-\underset{\|}{C}(Cl)-CH_3.$$

The high reactivity of 1,3-dichlorobut-2-ene depends primarily on the mobility of the allyl chlorine atom. Thus 1,3-dichlorobut-2-ene is readily hydrolysed and reacts with aromatic hydrocarbons, malonic and acetoacetic esters, ammonia and amines, sodium cyanide, thiocyanate salts, thiourea, etc.

The double bond in 1,3-dichlorobut-2-ene readily undergoes addition reactions and is ruptured by the action of oxidants. As was to be expected, the chlorine atom at the double bond cannot be substituted: both in 1,3-dichlorobut-2-ene itself and in its derivatives it can be removed as HCl by the action of alkali and sulphuric acid. In the first case an acetylenic compound or its isomerisation product is formed, and in the second a carbonyl compound (sulphuric acid hydrolysis):

$$-\underset{|}{\overset{Cl}{C}}=\underset{|}{\overset{H}{C}}- \rightarrow -\overset{O}{\overset{\|}{C}}-CH_2- + HCl.$$

Thus the possibilities of syntheses starting from 1,3-dichlorobut-2-ene are inexhaustable. The compounds formed (ethers, esters, amines, etc.) by the substitution of the

allyl chlorine atom with various groups can be of intrinsic interest and the compounds formed can serve as starting materials for the preparation of a wide variety of substances. Sulphuric acid hydrolysis, oxidation, and dehydrochlorination reactions have proved particularly fruitful. The present review deals with the main types of synthesis based on 1,3-dichlorobut-2-ene.

II. 3-CHLOROBUT-2-ENOL AND ITS ETHERS

The hydrolysis of 1,3-dichlorobut-2-ene to 3-chlorobut-2-enol in the presence of various alkaline reagents [Na_2SO_3, $NaHCO_3$, $Ca(OH)_2$] was first carried out by Klebanskii and Chevychalova[14]. The best yield of the chloro-alcohol is obtained with Na_2CO_3. This reaction was also studied in detail by Tishchenko[15]:

$$CH_3—CCl=CH—CH_2Cl \xrightarrow{H_2O} CH_3—CCl=CH—CH_2OH.$$

Akopyan and coworkers demonstrated that 3-chlorobut-2-enol is readily hydrogenated to butanol in the presence of Raney nickel[16]. Many workers showed that in the presence of CrO_3 3-chlorobut-2-enol is oxidised to β-chlorocrotonaldehyde[17,18], from which *trans*-β-chlorocrotonic acid[17] (catalytic oxidation), methylquinoline[18] (condensation with aniline), 4-methylpyridine[19] (condensation with guanidine), and other compounds were obtained.

3-Chlorobut-2-enol is dehydrochlorinated by alcoholic alkali to but-2-yn-1-ol,[12,17,20] which can be split by aqueous or powdered potassium hydroxide to yield methylacetylene[20]:

$$CH_3—C\equiv C—CH_2OH \xrightarrow{KOH} CH_3C\equiv CH+HCHO,$$

or oxidised by the chromic acid mixture to tetrolic acid (yield 35.8%)[17].

Sulphuric acid hydrolysis of 3-chlorobut-2-enol gives methyl vinyl ketone in 70% yield[21]:

$$CH_3CCl=CHCH_2OH \xrightarrow{16\%\ H_2SO_4} CH_3COCH=CH_2.$$

Ethers of 3-chlorobut-2-enol can be obtained both directly from 1,3-dichlorobut-2-ene and *via* the alcohol. 3-Chlorobut-2-enyl ethers of simple alcohols and phenols have been synthesised by the reaction of alkaline solutions of the latter with 1,3-dichlorobut-2-ene.[14,22-25] This reaction is quantitative and can be used for the determination of hydrolysable chlorine[26]. Mkryan showed that under the action of alcoholic alkali 3-chlorobut-2-enyl ethers split off HCl yielding acetylenic ethers[27], which are split by powdered potassium hydroxide into vinylacetylene and the corresponding alcohol or phenol[28]:

$$CH_3CCl=CH—CH_2Cl \xrightarrow[\text{alkali}]{ROH} CH_3CCl=CH—CH_2OR \xrightarrow[\text{alkali}]{}$$

$$\longrightarrow CH_3C\equiv C—CH_2OR \xrightarrow{KOH} CH_2=CH—C\equiv CH+ ROH.$$

Isagulyants and Azizyan obtained many 3-chlorobut-2-enyl ethers of phenyls and alcohols and investigated their oxidation[29-32]. They showed that, like 1,3-dichlorobut-2-ene itself[33], the ethers are oxidised at the double bond in the presence of potassium permanganate and nitric acid. Oxidation of the 3-chlorobut-2-enyl ethers of phenols gave the corresponding aryloxyacetic acids:

$$ArOCH_2CH=CClCH_3 \xrightarrow{O_2} ArOCH_2COOH,$$

where Ar = phenyl, *m*-cresyl, *p*-t-butyl, *o*-methoxy-, *o*-ethoxy-, and *o*- and *p*-nitro-phenyl, 2,4-dinitrophenyl, and *m*- and *p*-phenylene.

Phenoxy- and 2,4-dichlorophenoxy-acetic acids and other compounds of this series are known to be herbicides and active stimulators and regulators of plant growth. The proposed method of synthesis of aryloxyacetic acid is superior to others known because the use of chloroacetic acid is eliminated. Compounds of the type of carboxymethylcellulose[34,35], whose value in various branches of industry is well known, were obtained similarly by oxidation of 3-chlorobut-2-enyl ethers of cellulose[34,36].

Durgaryan and Titanyan showed that oxidation with perbenzoic acid of aryloxychlorobutenes, as well as other compounds containing the 3-chlorobut-2-enyl group, results in the formation of epoxybutanes[37]:

$$ROCH_2CH=CClCH_3 \xrightarrow{O} ROCH_2CH—CClCH_3,$$

where R = alkyl or phenyl.

Vartanyan and Tosunyan proposed a new method of synthesis of high-boiling solvents such as butyl ether, butyl cellosolve, dibutylcellosolve, butylcarbitol, and others, consisting in catalytic reduction (Ni, Pt) of the corresponding 3-chlorobut-2-enyl ethers under a pressure of 25 atm[38,39]:

$$CH_3CCl=CHCH_2Cl \xrightarrow[\text{alkali}]{ROH} CH_3CCl=CHCH_2OR \xrightarrow[Ni/Pt]{H_2} CH_3CH_2CH_2CH_2OR,$$

where

$$R=CH_3CH_2CH_2CH_2—,\ HOCH_2CH_2—,\ CH_3CH_2CH_2CH_2OCH_2CH_2—,\ HOCH_2CH_2OCH_2CH_2—.$$

Thus butanol can be replaced by 1,3-dichlorobut-2-ene in the synthesis of many valuable solvents.

By cyanoethylation of 3-chlorobut-2-enol the same workers obtained 2-cyanoethyl 3-chlorobut-2-enyl ether, whose hydrolysis gave the corresponding acid[40].

$$CH_3CCl=CHCH_2OH + CH_2=CHCN \xrightarrow{KOH} CH_3CCl=CHCH_2OCH_2CH_2CN.$$

Many alkoxymethyl 3-chlorobut-2-enyl ethers have been obtained in good yields (60–90%) by the reaction of 3-chlorobut-2-enol with various chloromethyl ethers[41]:

$$CH_3CCl=CHCH_2OH + ClCH_2OR \rightarrow CH_3CCl=CHCH_2OCH_2OR,$$

where R = H or isoalkyl (C_1–C_5).

III. 3-CHLOROBUT-2-ENYL ESTERS OF CARBOXYLIC ACIDS

Esterification of carboxylic acids with 3-chlorobut-2-enol was first investigated by Petrov[42]. In his search for herbicidal preparations, Dovlatyan synthesised the 3-chlorobut-2-enyl esters[43-48] and amides[48] of many carboxylic acids. The esters were synthesised in good yields both by esterification of the carboxylic acids with 3-chlorobut-2-enol and by the reaction of the carboxylic acid salts with 1,3-dichlorobut-2-ene in the presence of catalytic amounts of pyridine and other bases:

$$\left.\begin{matrix} RCOOH + CH_3CCl=CHCH_2OH \\ RCOOM + CH_3CCl=CHCH_2Cl \end{matrix}\right\rangle \rightarrow RCOOCH_2CH=CClCH_3,$$

where R = aryloxy, 1- and 2-naphthoxy, alkyl, chloromethyl, and trichloromethyl.

Among the esters synthesised, particular interest attaches to the 3-chlorobut-2-enyl ester of 2,4-dichlorophenoxyacetic acid (crotilin)[43,47]; herbicidal properties are

not inferior to those of the highly active butyl ester[49], whose preparation requires butanol. Crotilin has been successfully tested under field conditions in various agricultural regions of the USSR.[49-51] 3-Chlorobut-2-enyl 4-chloro- and 2-methyl-4-chloro-phenoxyacetates exhibit high herbicidal activity against broad-leaved weeds whilst 3-chlorobut-2-enyl trichloroacetate is active against gramineous weeds[44]. The 3-chlorobut-2-enyl-substituted amides of the same carboxylic acids, obtained in best yields by the reaction of 3-chlorobut-2-enylamine (see the section on amines) with the free acids, are unexpectedly without high herbicidal activity[48].

Gefter synthesised the 3-chlorobut-2-enyl esters of adipic, sebacic, thiodipropionic, and phthalic acids by reaction of these acids (the anhydride in the case of the phthalic acid) with 3-chlorobut-2-enol in the presence of *p*-toluenesulphonic acid[52].

Vartanyan and coworkers obtained bis(3-chlorobut-2-enyl) phthalate in a higher yield (70 instead of 50%) by the reaction of sodium phthalate with 1,3-dichlorobut-2-ene in the presence of catalytic amounts of pyridine[53]. The ester was isolated as a mixture of two stereoisomers (liquid and crystalline). Tests on the individual isomers and their mixtures showed that as plasticisers they are not inferior to dibutyl phthalate. Mixtures of phthalate esters and 3-chlorobut-2-enyl salicylate can also be of interest as plasticisers[53]. The possible use of 3-chlorobut-2-enyl esters of carboxylic acids as plasticisers is being intensely studied at present[54].

IV. CONDENSATION WITH AROMATIC HYDROCARBONS AND RELATED REACTIONS

Isagulyants and Mushegyan showed that 1,3-dichlorobut-2-ene readily reacts with aromatic hydrocarbons in the presence of $AlCl_3$ with the formation of 1-aryl-3-chlorobut-2-enes[55-58]:

$$CH_3CCl{=}CHCH_2Cl + ArH \rightarrow CH_3CCl{=}CHCH_2Ar,$$

where Ar = phenyl, *p*-tolyl, *p*-cumenyl, and 1-naphthyl. This reaction was carried out by other workers in the presence of metallic aluminium[59] and anhydrous $ZnCl_2$.[60] The product of the condensation of naphthalene with 1,3-dichlorobut-2-ene in the presence of $ZnCl_2$ has been suggested as a rubber plasticiser[61,62].

1-Aryl-3-chlorobut-2-enes have been used in various reactions. The corresponding ketones were obtained by the action of concentrated sulphuric acid[57]:

$$CH_3CCl{=}CHCH_2Ar \xrightarrow{H_2SO_4} CH_3COCH_2CH_2Ar.$$

Reaction of 1-aryl-3-chlorobut-2-enes with sodium ethoxide yields 1-arylbut-2-ynes and 1-aryl-3-ethoxybut-1-enes.[57] The formation of the latter can be explained by an alkali-catalysed 1,3-hydride shift placing the double bond in conjugation with the aromatic system:

$$CH_3CCl{=}CHCH_2Ar \xrightarrow{C_2H_5ONa} \left[CH_3CCl(H)CH{=}CHAr\right] \rightarrow CH_3CH(OC_2H_5)CH{=}CHAr.$$

When powdered potassium hydroxide in an inert solvent (benzene, toluene) is allowed to act on 1-aryl-3-chlorobut-2-enes, the latter undergo a similar reaction. The final products are 1-arylbuta-1,3-dienes and their dimers[63-67].

$$CH_3CCl{=}CH{-}CH_2Ar \xrightarrow{KOH} CH_2{=}CH{-}CH{=}CHAr,$$

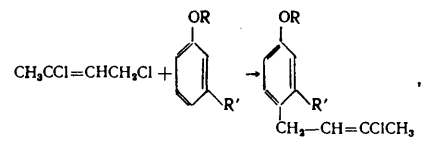
where Ar = phenyl, *p*-tolyl, *p*-cumenyl, 1-naphthyl, and *p*-phenoxyphenyl.

Oxidation of 1-aryl-3-chlorobut-2-ene with potassium permanganate yields the corresponding arylcarboxylic acids[56,58]. The reaction with perbenzoic acid gives substituted epoxybutanes as in the case of alkoxyphenoxy-3-chlorobut-2-enes and 1,3-dichlorobut-2-ene:[37]

$$CH_3CCl{=}CHCH_2Ar \xrightarrow{O} CH_3CCl(O)CHCH_2Ar.$$

2-Aminothiazole derivatives have been synthesised from the epoxybutanes by the action of thiourea[68].

Isagulyants and Azizyan showed that phenols and their ethers can also be reacted with 1,3-dichlorobut-2-ene in the presence of $AlCl_3$ giving 3-chlorobut-2-enyl derivatives[69]:



where R = H or C_2H_5 and R′ = H or CH_3. Condensation of *p*-(3-chlorobut-2-enyl)phenol with formaldehyde results in the formation of a transparent resin similar to the "100% resins".[69] In the presence of metal chlorides 1,3-dichlorobut-2-ene polymerises into film-forming substances[70]. Klebanskii *et al.*[71] investigated this reaction in detail and isolated both low-molecular-weight and high-molecular-weight polymerisation products, whose formation can be represented as follows:

$$CH_3CCl{=}CHCH_2Cl + FeCl_4^- \cdot {}^+CH_2CH{=}CClCH_3 \rightarrow$$

$$\rightarrow \left[CH_3CCl{=}HCCH_2{-}CH(CH_2Cl){-}{}^+CClCH_3 \cdot FeCl_4^-\right] \rightarrow CH_3CCl_2CHCH_2CH{=}CClCH_3 + FeCl_3. \quad \text{etc.}$$

When 1,3-dichlorobut-2-ene reacts under similar conditions with chloroprene[72], isoprene, or buta-1,3-diene[73], low-molecular-weight and high-molecular-weight compounds, probably telomerisation products, are also formed:

$$CH_3CCl{=}CHCH_2Cl + nCH_2{=}CXCH{=}CH_2 \rightarrow CH_3CCl{=}CHCH_2(CH_2CX{=}CHCH_2)_nCl,$$

where X = H. Cl, or CH_3.

V. REACTIONS WITH ORGANOMETALLIC COMPOUNDS

Reaction of 1,3-dichlorobut-2-ene with alkylmagnesium halides yields the corresponding substituted alkene[74-79]:

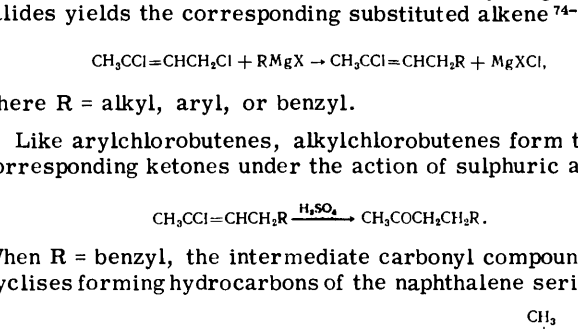
$$CH_3CCl{=}CHCH_2Cl + RMgX \rightarrow CH_3CCl{=}CHCH_2R + MgXCl,$$

where R = alkyl, aryl, or benzyl.

Like arylchlorobutenes, alkylchlorobutenes form the corresponding ketones under the action of sulphuric acid[41]:

$$CH_3CCl{=}CHCH_2R \xrightarrow{H_2SO_4} CH_3COCH_2CH_2R.$$

When R = benzyl, the intermediate carbonyl compound cyclises forming hydrocarbons of the naphthalene series[74-75]:

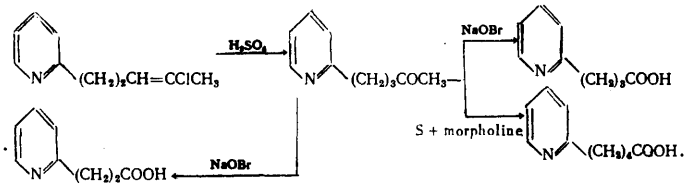


One of the communications from the Du Pont de Nemours Company[80] indicates the possibility of obtaining 2,7-dichloroocta-2,6-diene by allowing 1,3-dichlorobut-2-ene to react with metallic magnesium:

$$2CH_3CCl{=}CHCH_2Cl + Mg \rightarrow CH_3CCl{=}CH\cdot CH_2CH_2\cdot CH{=}CCl\cdot CH_3.$$

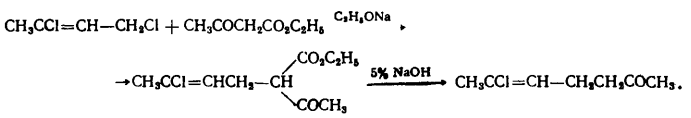
This compound was also prepared by Klebanskii and Vosik by the reaction of metallic magnesium with 1-iodo-3-chlorobut-2-ene synthesised by the action of potassium iodide on 1,3-dichlorobut-2-ene.[81]

The product of the reaction of 1,3-dichlorobut-2-ene with the sodium derivative of picoline can serve as the starting material for the preparation of a number of pyridyl derivatives of aliphatic acids[82]:

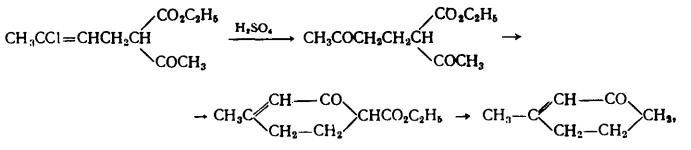


VI. SYNTHESES BASED ON THE PRODUCTS OF CONDENSATION OF 1,3-DICHLOROBUT-2-ENE WITH MALONIC AND ACETOACETIC ESTERS

As was to be expected, 1,3-dichlorobut-2-ene reacts particularly easily with acetoacetic ester, malonic ester, and other compounds containing an active methylene group. Wichterle and coworkers[83,84] and, independently, Isagulyants[85] obtained 3-chlorobut-2-enylacetoacetic ester whose ketone hydrolysis yielded 2-chlorohept-2-en-6-one:



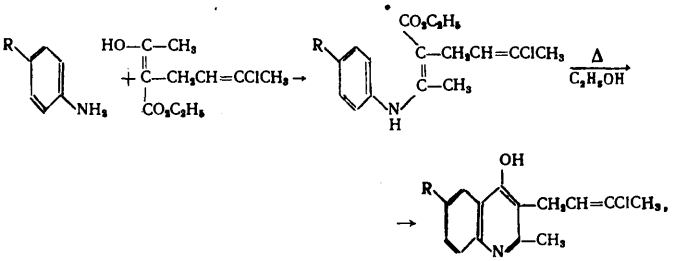
It has been shown that both the mono- and di-(3-chlorobut-2-enyl) derivatives of acetoacetic ester undergo sulphuric acid hydrolysis followed by cyclisation. The first derivative yields the ester of 4-methyl-2-oxocyclohex-3-en-1-carboxylic acid and a product of its ketone hydrolysis-1-methylcyclohex-1-en-3-one[83,84],



and the second derivative gives the di(3-oxobutyl)acetoacetic ester and the products of its subsequent cyclisation whose structure has not been reliably established[84-86].

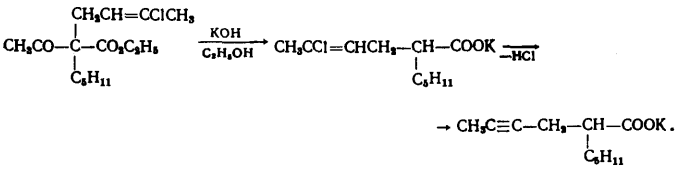
1-Methylcyclohex-1-en-3-one and its 5-alkyl derivatives were synthesised independently by Tatevosyan and coworkers[87-90], both by the same method as above and *via* the chloroheptenone. In particular, they obtained 5-isopropyl-1-methylcyclohex-1-en-3-one[89] (*d,l*-piperitone), which is used in the manufacture of terpenes.

Gyul'budagyan and coworkers obtained derivatives of 3-(3'-chlorobut-2'-enyl)-4-hydroxy-2-methylquinoline by the reaction of (3-chlorobut-2-enyl)acetoacetic ester with substituted anilines[91-93]:



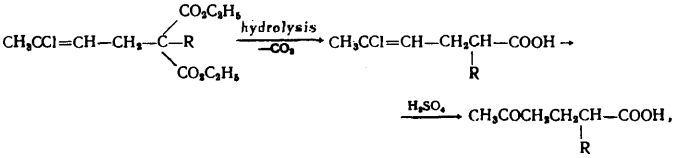
where R = H, alkyl, alkoxy, or CH_3CONH.

(3-Chlorobut-2-enyl)acetoacetic esters are convenient starting materials for the preparation of carboxylic acids of various structures. Thus acid hydrolysis of (3-chlorobut-2-enyl)isopentylacetoacetic ester followed by dehydrochlorination yields 2-(but-2'-ynyl)heptanoic acid[94]:



Acid hydrolysis of carboxymethyl-(3-chlorobut-2-enyl)-acetoacetic ester gave (3-chlorobut-2-enyl)succinic acid and its esters[95].

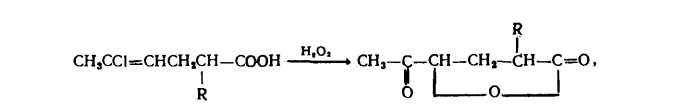
Tatevosyan and coworkers[96], and, independently, Wichterle[97] obtained 5-chlorohex-4-enoic acid by the hydrolysis of (3-chlorobut-2-enyl)malonic ester, sulphuric acid hydrolysis of the former yielding a keto-acid; this reaction was extended to alkyl-[98,99] and phenyl-(3-chlorobut-2-enyl)-malonic[100] esters:



where R = H, alkyl, or phenyl.

The chlorohexenoic and acetylbutyric acids obtained in this way can in turn be used as starting materials for various other syntheses. Thus 2-ethylhex-4-ynoic acid was obtained by the action of alcoholic potassium hydroxide on 5-chloro-2-ethylhex-4-enoic acid[98].

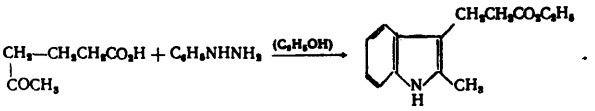
Dangyan and coworkers showed that the oxidation of the chlorohexenoic acid and its 2-substituted derivatives by hydrogen peroxide in formic or acetic acid yields δ-oxo-γ-lactones and therefore constitutes a convenient method for the synthesis of the latter[101-103]:



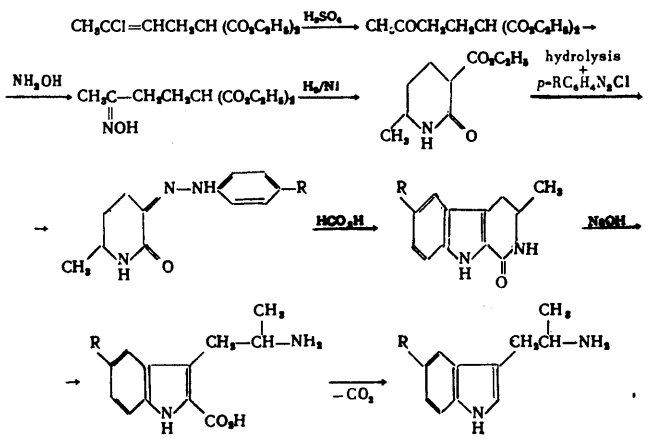
where R = H, alkyl, cyclohexyl, phenyl, benzyl.

γ-Acetylbutyric acid[104] and its α-substituted derivatives[105] readily condense with phenylhydrazine with the formation of esters of β-(2-methylindol-3-yl)propionic acid

which gave the corresponding hydrazides, indolylmercaptooxadiazoles[105], and indolylpropylamines[106] and their *N*-dialkyl derivatives[107]:

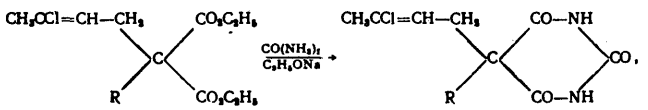


Other derivatives of indole, homologues of tryptamine and 5-methoxytryptamine with an α-methyl group in the ethylamine side chain, which are of special interest as biologically active substances (inhibitors of monoamino-oxidase)[108,109], have been synthesised from (3-chlorobut-2-enyl)malonic ester[109]:



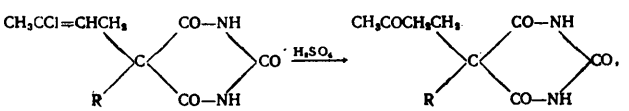
where R = H or OCH_3.

5-Alkyl-5-(3′-chlorobut-2′-enyl)- and 5,5-di(3′-chlorobut-2′-enyl)-barbituric acids have been synthesised by Tatevosyan and coworkers[110,111] and also by Wichterle and Němeček[112] by the reaction of urea with the corresponding malonic ester:



where R = alkyl or 3-chlorobut-2-enyl.

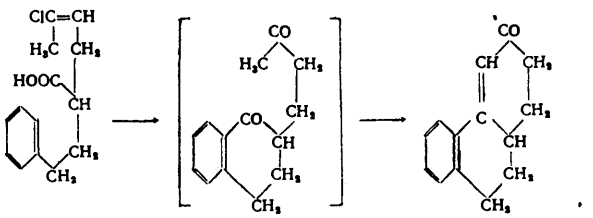
Contrary to expectation, these compounds had no soporific properties and proved to be toxic for animals[111]. The same applies to 5-ethyl-5-(3′-chlorobut-2′-enyl)thiobarbituric acid which was synthesised in a similar way[113,114]. Sulphuric acid hydrolysis of 3′-chlorobut-2′-enyl- and alkyl-(3′-chlorobut-2′-enyl)-barbituric acids gave the corresponding keto-derivatives[115]:



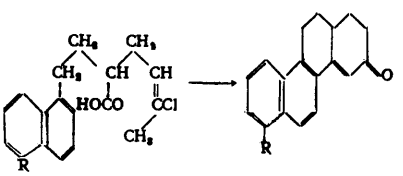
where R = H, alkyl, or cyclohexyl.

Tatevosyan and coworkers have made extensive studies on the synthesis of polycyclic hydroaromatic ketones, based on the sulphuric acid hydrolysis and subsequent double cyclisation of 3-chlorobut-2-enylarylalkanecarboxylic acids obtained from the corresponding arylalkyl-(3-chlorobut-2-enyl)malonic esters. The hydroaromatic ketones are used as starting materials for the synthesis of physiologically active compounds, in particular carcinogens, other known methods for the preparation of which are as a rule difficult.

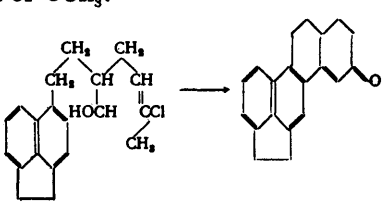
3-Oxo-1,2,3,9,10,10a-hexahydrophenanthrene was obtained in 75% yield by the action of sulphuric acid on α-(3-chlorobut-2-enyl)-γ-phenylbutyric acid[116]:



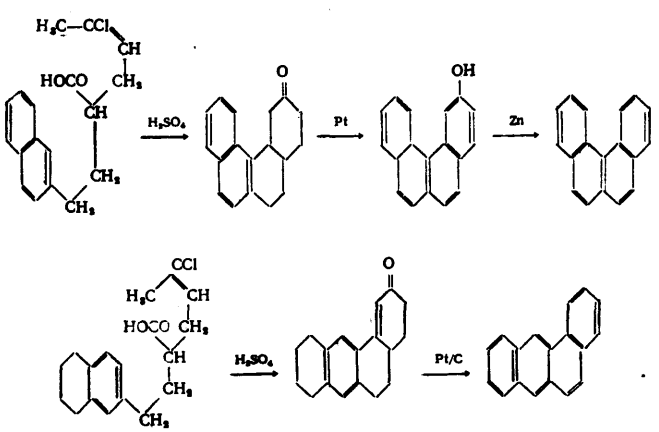
7-Methyl-,[117] 6-methyl-,[118] 6- and 7-methoxy-,[119] and 8-methyl- and 8-methoxy-3-oxo-1,2,3,9,10,10a-hexahydrophenanthrenes[120] were synthesised similarly. Ketones of the chrysene series were obtained by the action of sulphuric acid on α-(3-chlorobut-2-enyl)-γ-(1-naphthyl)-,[121] α-(3-chlorobut-2-enyl)-γ-(5-methoxynaphthyl)-,[122] and α-(3-chlorobut-2-enyl)-γ-(acenaphthyl)-butyric acids[123]:



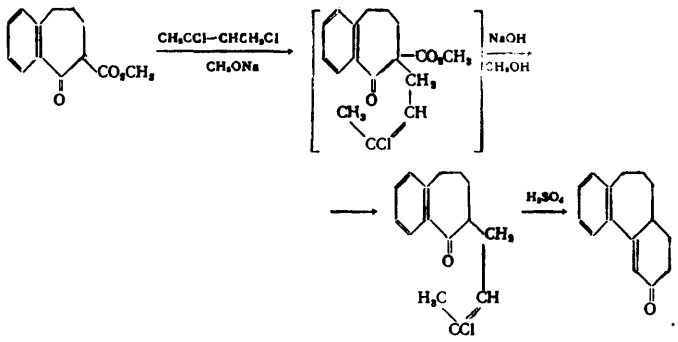
where R = H or OCH_3.



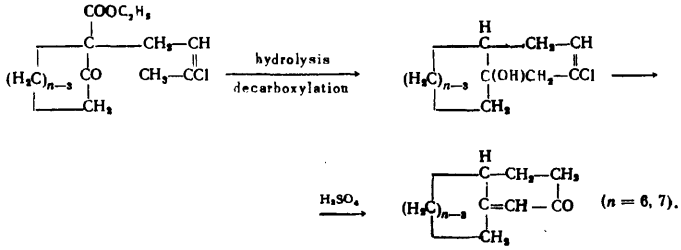
On reaction with sulphuric acid α-(3-chlorobut-2-enyl)-γ-(2-naphthyl)butyric acid yields ketones of the 3,4-benzophenanthrene series[124], while the 5,6,7,8-tetrahydronaphthyl derivatives give the ketones of the 1,2-benzophenanthrene series[125]. The corresponding benzophenanthrenes can be obtained by the dehydrogenation of these ketones:



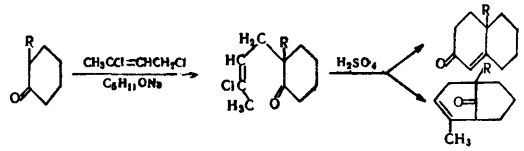
2-Oxo-2,3,4,4a,6,7-hexahydro-5*H*-dibenzo[*a*,*c*]cycloheptatriene can be synthesised by two-stage cyclisation of α-(3-chlorobut-2-enyl)-δ-phenylvaleric acid. However, it is obtained in best yield from benzosuberone [126]:



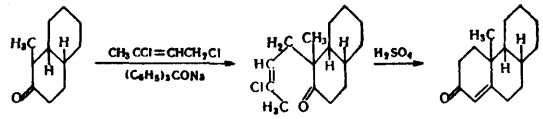
A similar cyclisation was carried out by Prelog *et al.* in the case of 2-(3′-chlorobut-2′-enyl)-2-ethoxycarbonylcyclic ketones [127]:



Julia studied the synthesis of some keto-derivatives of bicyclo[1,3,3]-nonene and hexahydronaphthalene from the products of the condensation of 1,3-dichlorobut-2-ene with cyclohexanone, 2-methylcyclohexanone, and isophorone [128–130]:



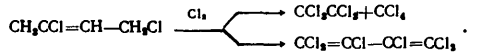
A similar cyclisation was achieved by Pinder and Robinson starting from the products of the condensation of 1,3-dichlorobut-2-ene with 1-methyl-*cis*-2-decalone [131]:



VII. SYNTHESIS OF CHLORINATED HYDROCARBONS

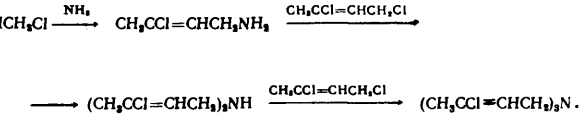
Carothers and coworkers showed that chlorination of 1,3-dichlorobut-2-ene in carbon tetrachloride and in the absence of solvent results in a complex mixture of chloro-derivatives [132,133]. At 40–60° the main product of the reaction is 1,2,3,3-tetrachlorobutane and at low temperatures 1,2,3-trichlorobut-3-ene and 1,2,3,3,4-pentachlorobutane. On dehydrochlorination of 1,2,3-trichlorobut-3-ene in the presence of alcoholic potassium hydroxide, 2,3-dichlorobuta-1,3-diene is formed while dehydrochlorination of 1,2,2,3,4-pentachlorobutane yields 1,2,3-trichlorobuta-1,3-diene [134,135], which on copolymerisation with chloroprene gives rubberlike products [135]. Klebanskii and coworkers made a detailed study of the above reactions and established the optimum conditions for the preparation of both chlorination and dehydrochlorination products [136].

Chlorination of 1,3-dichlorobut-2-ene at a high temperature (400–500°) in the presence of activated carbon yields carbon tetrachloride and hexachloroethane [137], whereas in the absence of catalyst hexachlorobuta-1,3-diene is formed [138]. The last compound has been proposed as an anti-phylloxera agent:



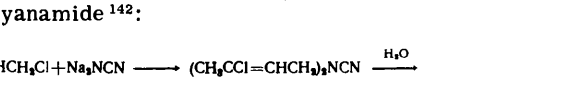
VIII. SYNTHESIS OF NITROGEN-CONTAINING COMPOUNDS

Wichterle and Hudlický showed that reaction of 1,3-dichlorobut-2-ene with aqueous ammonia (even in the presence of a large excess of the latter) yields predominantly the tertiary amine, whereas in liquid ammonia the primary and secondary amines are formed [139]:



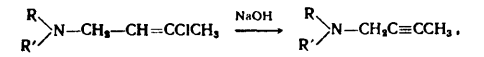
Babayan and Grigoryan synthesised these amines in ethanol and showed that the principal reaction product can be the primary, secondary, or tertiary amine depending on the conditions (temperature, excess of ammonia) [140]. Japanese workers have described a similar method of preparing 3-chlorobut-2-enylamines [141].

The secondary amine can be obtained by the hydrolysis of the product of condensation of 1,3-dichlorobut-2-ene with sodium cyanamide [142]:



The hydrogen atoms in primary and secondary amines [139–141, 143–152], in amides [139,153,154], imides [155], and sulphonamides [156] are just as easily substituted.

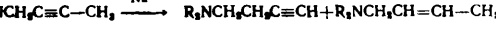
Dehydrochlorination of 3-chlorobut-2-enylamines was studied by Babayan and coworkers, who established that dialkyl- [144,157] and diaryl-3-chlorobut-2-enyl amines [149], as well as di- and tri-(3-chlorobut-2-enyl)amines [149], give the corresponding acetylenic amines when acted upon by alkali:



where

R=H, R′=$CH_3CH=CCl-CH_3$ (91.8%);
R=R′=$CH_3CH=CCl-CH_3$ (89.6%); R=R′=C_6H_5 (62.15%).

Under the action of metallic sodium these compounds are very readily isomerised to but-1-ynylamines, but-2-enylamines being formed at the same time [158]:



A very convenient method of synthesising acetylenic amines was proposed on the basis of these data [157]:

$$R_2NCH_2CH{=}CClCH_3 \xrightarrow{NaOH} R_2NCH_2C{\equiv}C{-}CH_3 \xrightarrow{Na} \longrightarrow R_2NCH_2CH_2C{\equiv}CNa \xrightarrow{CH_3I} R_2NCH_2CH_2C{\equiv}C{-}CH_3, \text{ etc.}$$

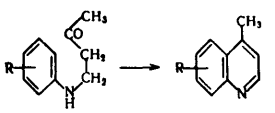
Dialkylbut-1-ynyl- and dialkylbut-2-enyl-amines are very convenient raw materials for the synthesis of various halogenated dialkylamino-derivatives of butane and butene [159,160].

3-Chlorobut-2-enylamine [139] and other amines containing only one 3-chlorobut-2-enyl group [144,145,161] form the corresponding aminobutanones when acted upon by concentrated sulphuric acid:

$$CH_3CCl{=}CHCH_2NRR' \xrightarrow{H_2SO_4} CH_3COCH_2CH_2NRR',$$

where R, R' = H, alkyl, or aryl.

Vavrečka [143] and, independently, Babayan and coworkers [161,162] showed that in the presence of $FeCl_3$ and other catalysts arylaminobutanones readily cyclise into lepidines:



The lepidines can also be obtained under conditions in which butynylamines are hydrated [146,163].

According to the data of Wichterle and Hudlický, amines and amides containing two [139] and three [164] 3-chlorobut-2-enyl groups are cyclised under conditions of sulphuric acid hydrolysis, di-(3-chlorobut-2-enyl)amines and the corresponding amides of carboxylic and sulphonic acids being converted into tetrahydropyridine derivatives:

$$RN(CH_2CH{=}CClCH_3)_2 \xrightarrow{H_2SO_4} \left[RN(CH_2CH_2COCH_3)_2\right] \longrightarrow RN\begin{cases}CH_2{-}CH_2\\ CH_2{-}C{=}CH_2\\ \qquad\quad |\\ \qquad\quad COCH_3\end{cases},$$

where R = H, alkyl, acyl, benzyl, or *p*-toluenesulphonyl.

Tri-(3-chlorobut-2-enyl)amine forms a bicyclic compound under these conditions.

With 3-chloro-1-dimethylaminobut-2-one as an example, it has been shown that 3-chlorobut-2-enylamines are readily chlorinated in hydrochloric acid solution forming trichloro-derivatives, which by dehydrochlorination and further chlorination can be converted into di- and tetra-chloro-derivatives [165]:

$$(CH_3)_2NCH_2CH{=}CClCH_3 \xrightarrow[HCl]{Cl_2} (CH_3)_2NCH_2CHClCCl_2CH_3 \xrightarrow{KOH} \longrightarrow (CH_3)_2NCH_2CCl{=}CClCH_3 \xrightarrow[HCl]{Cl_2} (CH_3)_2NCH_2CCl_2CCl_2CH_3.$$

Among other reactions of 3-chlorobut-2-enyl derivatives that of (3'-chlorobut-2'-enyl)-2,5-dimethylpiperidin-4-ol with benzoyl chloride is of interest [166], since the resulting benzoate, like other compounds of this series [151], may possess anaesthetic properties.

Babayan and coworkers have made extensive studies on quaternary ammonium compounds, in particular those with a 3-chlorobut-2-enyl group. They established from reactions of many compounds that quarternary salts containing 3-chlorobut-2-enyl or butynyl groups are readily split on heating with aqueous alkali into dienes (enynes) and the tertiary amine [167,168]:

$$R_3\overset{+}{N}\underset{Cl^-}{} CH_2CH{=}CClCH_3 + NaOH \xrightarrow[80-90^\circ]{H_2O} R_3N + CH_2{=}CH{-}C{\equiv}CH + CH_2{=}CCl{-}CH{=}CH_2.$$

This reaction constitutes a convenient method for the preparation of dienes and enynes on the one hand and tertiary amines on the other. The dehydrochlorination of quaternary ammonium salts containing a 3-chlorobut-2-enyl group can be achieved by the action of alkali at a lower temperature [168] and takes place much more readily than in the case of the tertiary amines [144].

Thermal degradation of ammonium salts containing a 3-chlorobut-2-enyl group results in the formation of chloroprene as well as 1,3-dichlorobut-2-ene [169,170]:

$$R_3\overset{+}{N}\underset{Cl^-}{} CH_2CH{=}CClCH_3 \longrightarrow \begin{cases} R_3N + HCl + CH_2{=}CCl{-}CH{=}CH_2\\ R_3N + CH_3CCl{=}CHCH_2Cl \end{cases}.$$

The first reaction is similar to the splitting of quaternary ammonium salts by alkali and can be used for the preparation of both the diene and tertiary amines.

Primary and secondary amines can be readily alkylated by quaternary ammonium salts containing a 3-chlorobut-2-enyl group [145] or even by 1,3-dichlorobut-2-ene itself in the presence of catalytic quantities of the quaternary ammonium salts [171] (*N*-alkylation). Other compounds containing a mobile hydrogen atom are alkylated similarly: acetoacetic ester, malonic ester, phenylacetylene, acetylacetone [172], bis(diphenylsulphonyl)methane [173] (*C*-alkylation), phenols and alcohols [173-175] (*O*-alkylation), and mercaptans and thiophenols [173] (*S*-alkylation).

In the reaction of di-(3-chlorobut-2-enyl)dimethylammonium chloride with tertiary amines containing an *N*-methyl group, the latter is exchanged for a 3-chlorobut-2-enyl group [176]. This transalkylation reaction makes it possible to replace secondary amines, in the synthesis of tertiary amines, by the more readily available tertiary amines (for example methylaniline can be replaced by dimethylaniline).

Among other nitrogen-containing compounds obtained from 1,3-dichlorobut-2-ene, 3-chlorobut-2-enyl cyanide is of interest. The first description of its preparation by the reaction of 1,3-dichlorobut-2-ene with sodium cyanide and its hydrolysis to the corresponding amide is given in a brief communication by Azatyan and Arakelyan [177]:

$$CH_3CCl{=}CHCH_2Cl \xrightarrow{NaCN} CH_3CCl{=}CHCH_2CN \longrightarrow CH_3CCl{=}CHCH_2CH_2NH_2.$$

Vartanyan showed that alcoholysis of 3-chlorobut-2-enyl cyanide with ethanol in the presence of sulphuric acid followed by sulphuric acid hydrolysis of the resulting chloropentenoate ester yields the corresponding ester of levulinic acid [178]. Hydrolysis of the nitrile with hydrochloric acid gives a number of levulinate esters in good yields [179]:

$$CH_3CCl{=}CHCH_2CN \xrightarrow[HCl]{ROH} CH_3CCl{=}CHCH_2{-}C\begin{cases}O\\ OR\end{cases} \xrightarrow{H_2SO_4} CH_3COCH_2CH_2C\begin{cases}O\\ OR'\end{cases},$$

where R = CH_3, C_2H_5, C_3H_7, C_4H_9, iso-C_4H_9, or iso-C_5H_{11}. Fetizon and Julia obtained levulinic acid in a similar way — by sulphuric acid hydrolysis of the chloropentenoic acid [180].

IX. DEHYDROCHLORINATION OF 1,3-DICHLOROBUT-2-ENE

The dehydrochlorination of 1,3-dichlorobut-2-ene was studied particularly thoroughly, since the aim was to recover and return to the manufacturing process the main reaction product — chloroprene or even the initial vinylacetylene.

The first investigations on these lines were carried out by Klebanskii and coworkers [14,181], who showed that 1,3-dichlorobut-2-ene is dehydrochlorinated to chloroprene in satisfactory yield by fused potassium hydroxide and by being passed over a copper catalyst at 250–300° (or better at 350–400°) in the presence of water vapour [181]:

$$ClCH_2{-}CH{=}CCl{-}CH_3 \xrightarrow{-HCl} CH_2{=}CCl{-}CH{=}CH_2.$$

There are indications that the dehydrochlorination can be carried out at a higher temperature (530°) in the absence of catalyst [182].

The dehydrochlorination of 1,3-dichlorobut-2-ene in the presence of potassium hydroxide in ethylene glycol has been proposed as a laboratory method for the preparation of vinylacetylene (50% yield) [183]:

$$ClCH_2{-}CH{=}CCl{-}CH_3 \xrightarrow[-2HCl]{} CH_2{=}CH{-}C{\equiv}CH.$$

As mentioned above, Babayan and coworkers showed that, in the alkaline [167,168] and thermal [169,170] degradation of quaternary salts containing a 3-chlorobut-2-enyl group, chloroprene and vinylacetylene are formed together with the tertiary amine.

X. SYNTHESIS OF SULPHUR-CONTAINING COMPOUNDS

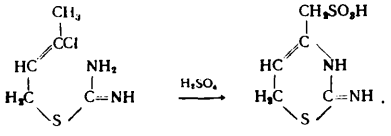
Products of the condensation of alkyl halides with thiourea — *S*-substituted isothioureas (thiuronium salts) — are convenient starting materials for the preparation of various organosulphur compounds. The product of the condensation of 1,3-dichlorobut-2-ene with thiourea — *S*-(3-chlorobut-2-enyl)isothiourea hydrochloride — was described for the first time by Procházka and Wichterle [184] and, independently, by Esayan and Sarkisyan [185]:

$$CH_3CCl{=}CHCH_2Cl + SC(NH_2)_2 \longrightarrow CH_3CCl{=}CHCH_2S{-}C(=NH)NH_2 \cdot HCl.$$

Recently, it has been shown that this compound is an active defoliant desiccant of the cotton plant [186]. Its hydrolysis gave 3-chlorobut-2-enethiol [184], which can be obtained directly from 1,3-dichlorobut-2-ene by its reaction with sodium hydrosulphide [184,187]:

$$CH_3CCl{=}CHCH_2S{-}C(=NH)NH_2 \cdot HCl \xrightarrow{H_2O(NaOH)} CH_3CCl{=}CHCH_2SH.$$
$$CH_3CCl{=}CHCH_2Cl \xrightarrow{NaHS}$$

When *S*-(3-chlorobut-2-enyl)isothiourea is subjected to sulphuric acid hydrolysis, a crystalline product is formed [184,188]:



Chlorination of the *S*-thiourea derivatives in an aqueous medium yields 3-chlorobut-2-enesulphonyl chloride, whose hydrolysis in an alkaline medium gives the 3-chlorobut-2-enesulphonate [185].

$$CH_3CCl{-}CHCH_2S{-}C(=NH)NH_2 \cdot HCl \xrightarrow{Cl_2+H_2O} CH_3CCl{=}CHCH_2SO_2Cl \xrightarrow[H_2O]{NaOH} CH_3CCl{=}CH.$$

The last compound is obtained in a better yield by the reaction of 1,3-dichlorobut-2-ene with SO_2 in an alkaline medium. The resulting mixture of *cis*- and *trans*-stereoisomers was separated by fractional crystallisation [189]. A keto-sulphonic acid is formed on sulphuric acid hydrolysis of this compound [189,190]:

$$CH_3CCl{=}CHCH_2SO_3Na \xrightarrow{H_2SO_4} CH_3COCH_2CH_2SO_3H.$$

Under the same conditions 3-chlorobut-2-enesulphonyl chloride splits into methyl vinyl ketone, SO_2, and HCl: [190]

$$CH_3CCl{=}CHCH_2SO_2Cl \xrightarrow{H_2SO_4} \left[CH_3COCH_2CH_2SO_2Cl\right] \longrightarrow CH_3COCH{=}CH_2 + SO_2 + 2HCl.$$

Halogenation of sodium 3-chlorobut-2-enesulphonate in an aqueous medium yields crystalline products [185,189,191], which Exner and Wichterle convincingly showed to be sulphones [189]:

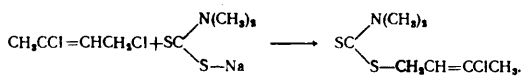
$$CH_3CCl{=}CHCH_2SO_3Na \xrightarrow[(H_2O)]{X_2} CH_3{-}\underset{\displaystyle O\ CH_3}{\overset{\displaystyle X\ X}{C{-}CH}}.$$
$$\qquad\qquad\qquad

with Na_2S. Allyl-(3-chlorobut-2-enyl) sulphide was synthesised similarly. Reaction of 1,3-dichlorobut-2-ene with Na_2S_2 yielded di-(3-chlorobut-2-enyl) disulphide, also as a mixture of two stereoisomers [200].

3-Chlorobut-2-enylmercaptoacetic acid was synthesised by the reaction of 1,3-dichlorobut-2-ene with mercaptoacetic acid in the presence of sodium hydroxide. It was then used to prepare 3-chlorobut-2-enylmercaptopenicillin, which proved to have antibiotic activity [201]. Other interesting sulphides derived from 1,3-dichlorobut-2-ene are products of the condensation of the latter with polysulphides, which have been proposed as softeners for varnishes and rubber [202].

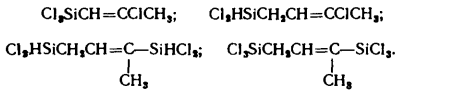
Among other sulphur-containing derivatives of 1,3-dichlorobut-2-ene, 3-chlorobut-2-enyl thiocyanate has been investigated in detail. This compound is readily obtained by the reaction of 1,3-dichlorobut-2-ene with a thiocyanate salt in an alcoholic [184] or aqueous alcoholic [203] medium. It has high insecticidal and acaricidal activity [203].

3-Chlorobut-2-enyl *NN*-dimethyldithiocarbamate, which may prove to be of interest as a fungicide, nematocide, and herbicide, was synthesised [204] by the reaction of 1,3-dichlorobut-2-ene with sodium *NN*-dimethyldithiocarbamate, as part of a series of syntheses of carbamates containing a 3-chlorobut-2-enyl group (analogues of the well-known insecticide Sevin):

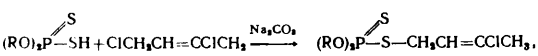


XI. SYNTHESIS OF ORGANOMETALLIC AND ORGANOMETALLOID COMPOUNDS

Among compounds of this type containing a 3-chlorobut-2-enyl group, those of silicon and phosphorus are known. Sadykh-Zade and Petrov showed that when 1,3-dichlorobut-2-ene is heated in a glass tube with an Si–Cu alloy, a complex mixture of chlorosilanes is formed [205], the following having been isolated in a pure state by fractional distillation:

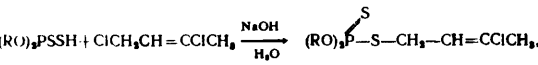


In his attempts to obtain insecticidal preparations, Tichý synthesised a series of *OO*-dialkyl *S*-(3-chlorobut-2-enyl) phosphorothiolothionates [206]:

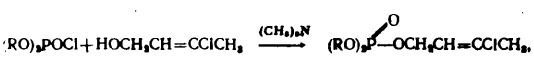


where R = CH_3, C_2H_5, n-C_3H_7, or n-C_4H_9. According to his data, these compounds are less active than the well-known insecticide (acaricide) diethyl *p*-nitrophenyl phosphorothionate (Thiophos, Parathion).

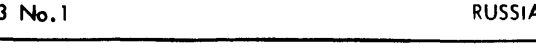
Apart from the phosphorothiolothionates, dialkyl 3-chlorobut-2-enyl phosphates, phosphorothionates, and phosphorothiolates have been synthesised at the Institute of Organoelemental Compounds of the USSR Academy of Sciences [207]:



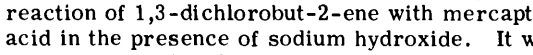
where R = CH_3 (74%), C_2H_5 (85%), or iso-C_3H_7 (67%);



where R = C_2H_5 (60%);



where R = C_2H_5 (60%) or iso-C_3H_7 (68%);



where R = C_2H_5 (35%). The compounds exhibit insecticidal activity on contact. The phosphorothionates and phosphorothiolates are the most active.

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The syntheses based on 1,3-dichlorobut-2-ene described above show that the latter can find a wide variety of applications both in industry and in preparative organic chemistry.

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THEORY OF CATALYTIC HYDROGEN WAVES IN ORGANIC POLAROGRAPHY

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I. INTRODUCTION

Catalytic hydrogen waves are an interesting phenomenon, frequently encountered in polarographic practice. They are associated with certain substances whose function is a catalytic one, since they assist the evolution of molecular hydrogen at the cathode without being altered by the electrode process. Catalytic hydrogen waves are observed at potentials less negative than the normal hydrogen waves for the given solution. The catalysts effectively lower the hydrogen overvoltage, thus accelerating (or catalysing) the evolution of hydrogen and justifying the use of the term "catalytic hydrogen waves".

Studies of catalytic waves can yield the rate constants for fast protolytic reactions, they can clarify adsorption phenomena at very low surface coverages, assess the rate of bimolecular free radical interactions, and quantitatively characterise the relationship between the structure of organic catalysts and their catalytic activity.

Catalytic hydrogen waves have also a practical interest. When applied to analytical problems, they enable conventional polarographic apparatus to be operated at the 10^{-7} M level, *i.e.* they raise the sensitivity of classical polarography by 2–3 orders of magnitude. The biological and medical applications of catalytic hydrogen waves are particularly interesting: they have made possible a number of diagnostic procedures such as Brdička's well-known serological polarographic test for cancer.

Herles and Vančura, in 1930, were the first to observe an unusual wave whilst studying the polarograms of blood serum solutions with sodium, potassium, and magnesium salts as supporting electrolytes. A report of these experiments was published, as a short communication[1], in 1932. Heyrovský and Babička repeated the work in 1930, and confirmed the appearance of new waves when proteins were

present in an ammoniacal base solution. The waves were shown to be associated with catalytic evolution of hydrogen, and not with reduction of the proteins[2].

Brdička later discovered[3] that the catalytic effect of proteins and of other sulphur compounds is greatly enhanced by the addition of divalent or trivalent cobalt salts to the ammoniacal buffer solution.

At about the same time Pech observed[4] that catalytic hydrogen waves can also be induced by organic compounds not containing sulphur, such as alkaloids. Since then, a great deal of work has been devoted to the study of catalytic hydrogen waves due to proteins in ammoniacal buffer solutions containing cobalt salts, and waves in solutions of alkaloids and other nitrogen derivatives (see, for example, the literature surveys given in Refs. 5–11). Much experimental information is available in the papers by Kirkpatrick[11], Stromberg *et al.*[12,13], Knobloch[14,15], Kůta and Drabek[16], von Stackelberg *et al.*[17–19], Nürnberg[20], Lamprecht *et al.*[21], and many other workers.

1. Features of Catalytic Hydrogen Waves

Catalytic waves are quite different from the normal, diffusion-limited, polarographic waves. Catalytic limiting currents do not obey the Ilkovič equation; they frequently have very high or very low temperature coefficients; they do not (as a rule) depend on the height of the mercury column above the dropping electrode, but occasionally, and in contrast with diffusion currents, they increase as the height of the mercury column decreases. The shape of catalytic hydrogen waves is always different from that of diffusion-limited waves; the limiting currents and the half-wave potentials of catalytic waves show a complicated dependence on the catalyst concentration and on the composition of the solution.

2. Effect of Catalyst Concentration and Solution Composition on the Catalytic Limiting Current

The effect of catalyst concentration (c_{cat}) and solution composition on the height of catalytic hydrogen waves has been discussed in a large number of papers. It has been shown that the catalytic limiting current increases linearly with c_{cat} at first, but the initial proportionality is not maintained, and at very high values of c_{cat} the limiting current approaches a constant value. This behaviour was first observed by Brdička[22] in his work on the catalytic hydrogen waves of egg albumin in unbuffered solutions of KCl, and on albumin waves in buffered solutions of different compositions and pH. Brdička found that the height of the catalytic wave and its limiting value at high catalyst concentrations are both increased by raising the buffer capacity of the solution and by lowering the pH.

Brdička derived the following empirical relation[22] between limiting current and cobalt ion concentration for catalytic waves in protein solutions containing cobalt salts:

$$i_{lim} = K\,[Co^{2+}]^{0.74}.$$

The concept of catalyst regeneration after the electrode process, developed in Brdička's papers, is an important one, and was adopted in subsequent theories of catalytic hydrogen waves. According to Brdička, regeneration consists in addition of hydrogen ions to the product of electrochemical discharge of the catalyst under the influence of acids (proton donors).

Stromberg also reported[12] an increase in the catalytic wave with increasing concentration of proteins and cobalt salts, and interpreted this phenomenon in terms of the kinetics of the electrode reaction, finally arriving at an expression for the limiting current of the catalytic wave. Klumpar[23] put forward an empirical formula for the catalytic limiting current in terms of the concentration of cystine and cobalt salt in the solution.

Knobloch[14] made the first detailed studies of the influence of various factors on the catalytic hydrogen waves produced by nitrogen compounds (such as pyridine derivatives) in buffered solutions free from cobalt salts. He showed that the limiting current of a catalytic hydrogen wave is increased by decreasing the pH of the solution and by increasing its buffer capacity. In view of the similarity between the observed current–catalyst concentration curve and the Langmuir adsorption isotherm, Knobloch suggested that the current is limited by the amount of catalyst adsorbed on the surface, and identified the maximum current obtained at high catalyst concentrations with complete coverage of the electrode surface by catalyst particles. The influence of pH and buffer capacity is explained in terms of protolytic regeneration of the catalytically active cationic form of the catalyst: this process is also thought to bring about a decrease in hydrogen overvoltage by Heyrovský's mechanism, *i.e.* by increasing the rate of formation of H_2^+ molecule-ions from H and from the protons of the cationic form of the catalyst. Thus, Knobloch was the first to ascribe electrochemical activity only to the acidic (or cationic) form of nitrogen-containing catalysts.

The effect of catalyst concentration and proton donor concentration on catalytic hydrogen waves has been studied in detail[24,25] by examining the first quinine wave in solutions containing effectively only one proton donor — hydrochloric acid — and a supporting electrolyte of 1 *N* LiCl. As in other catalytic hydrogen waves, the catalytic current in quinine solutions increases with quinine concentration in a way (Fig. 1) reminiscent of the Langmuir adsorption isotherm. The asymptotic values of the wave height, and,

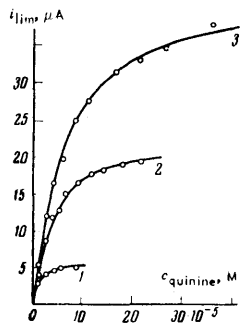

Fig. 1. Variation of limiting catalytic current with quinine concentration at different concentrations of hydrochloric acid (10^{-3} M): 1) 1.06; 2) 3.65; 3) 6.8.

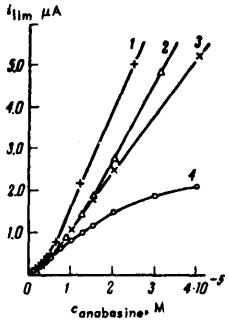

Fig. 2. Variation of limiting catalytic hydrogen current with anabasine concentration in acetate buffer solutions of ionic strength $I = 0.5$: 1) pH 4.46, $\Sigma c_{ac} = 0.2$ M; 2) pH 5.0, $\Sigma c_{ac} = 0.1$ M; 3) pH 5.0, $\Sigma c_{ac} = 0.2$ M; 4) pH 6.0, $\Sigma c_{ac} = 0.1$ M.

even more important, the quinine concentrations at which i_{lim} approaches the asymptote, were found[25] to depend on the concentration of hydrochloric acid in solution: the lower the concentration of HCl, the lower the limiting wave height, and the lower the quinine concentration needed to approach this limiting value (Fig. 1).

Hence, the limiting wave height is not due to full coverage of the surface of adsorbed catalyst. By comparing the limiting height of the catalytic wave with the diffusion current for hydrogen ion discharge, it can be shown that this limit arises from complete exhaustion of proton donors (in this case hydrogen ions) at the electrode surface. Its value corresponds to the limiting rate of supply of hydrogen ions by diffusion from the bulk solution to the electrode surface[24,25].

In the presence of an excess of proton donors and very low concentrations of catalyst, the height of the catalytic wave shows an unusual dependence on the concentration of catalyst in solution, increasing faster than linearly with catalyst concentration (see, for example, Fig. 2, taken from Ref. 26). This is a fairly frequent phenomenon: thus, some of the polarograms given in Kirkpatrick's paper[11] show catalytic hydrogen waves, for atropine and pilocarpine in buffer solutions, whose height increases faster than the alkaloid concentration.

The present writer, after examining available experimental data in the light of the ideas of Brdička, Knobloch, and Stromberg, put forward[24,27] a mechanism of catalytic hydrogen evolution which explains all the experimental facts. Equations which adequately describe the observed phenomena were derived by combining this scheme with Brdička and Wiesner's well-known views on the kinetics of current limitation, with Frumkin's theoretical considerations of the influence of double layer structure on electrode processes and of the mechanism by which organic substances are adsorbed at an electrode, and lastly with Delahay and Feike's data on adsorption kinetics.

3. Mechanism of Catalytic Hydrogen Waves in Solutions of Organic Bases

Catalytically active organic substances invariably exist in two forms: the acid form BH^+ and the basic form B (in the Brønsted sense), which are in mutual protolytic equilibrium:

$$B + DH^+ \underset{\beta\sigma}{\overset{\rho}{\rightleftharpoons}} BH^+ + D. \qquad (I)$$

The symbol DH^+ stands for the acids (proton donors) present in solution, D for their conjugate bases.

Various organic compounds catalyse hydrogen evolution by virtue of an unshared electron pair (*e.g.* on an atom of nitrogen, sulphur, oxygen, phosphorus, arsenic, etc.) which can add on a proton to give an 'onium' compound able to react electrochemically at the cathode. The electrochemical activity of 'onium' compounds arises not from their positive charge (which assists the movement of species towards the cathode, and their discharge[28]) but, rather, from the very nature of the 'onium' ion. If electron transfer to a protonated 'onium' form were due exclusively to the positive charge on the latter, the same process should occur, albeit at a more negative (200–300 mV) potential, even with the uncharged, unprotonated form of the catalyst. This is observed with charged and uncharged derivatives of aniline and phenol[29-31], and also with weak acids and their anions (see, for example, Refs. 32–40). However, electrons are not transferred to the unprotonated form of the catalyst, which justifies the above conclusion.

The catalytic activity of organic compounds is also unrelated to the mobility of hydrogen ions within the molecule: careful studies[18] of compounds in which the hydrogen is very labile have failed to reveal any catalytic activity.

Electron transfer to the protonated form of the catalyst

$$BH^+ + e^- \underset{\longleftarrow}{\overset{\text{electrode}}{\longrightarrow}} BH \qquad (II)$$

results in an unstable, uncharged species behaving like a free radical.

In the discharge of tetrasubstituted ammonium[41-43] or phosphonium[44] salts, or of trisubstituted sulphonium cations[45], the unstable products can dimerise, as is the case with *N*-alkylpyridinium salts[46-49], or alternatively they can be attacked at the carbon–heteroatom bond, giving the corresponding tertiary amines, phosphines, or sulphides respectively, as well as hydrocarbon radicals. The latter can be reduced at the cathode, react with the solvent, dimerise, or disproportionate.

When a protonated 'onium' cation is discharged, as in the catalytic evolution of hydrogen by the species BH (see reaction scheme II), the bimolecular reaction

$$2BH \xrightarrow{k_d} 2B + H_2 \qquad (III)$$

is apparently energetically more favourable than the splitting off of a hydrocarbon radical or a hydrogen atom, since it regenerates the catalyst in its basic form, and evolves molecular hydrogen. Because the reaction is bimolecular, its rate decreases very significantly with decrease in catalyst concentration, and can, in some cases, limit the rate of the overall process. This situation can arise under the conditions of the experiments summarised in Fig. 3. Reports[11,24,26] of a limiting catalytic current increasing faster than linearly with catalyst concentration can be

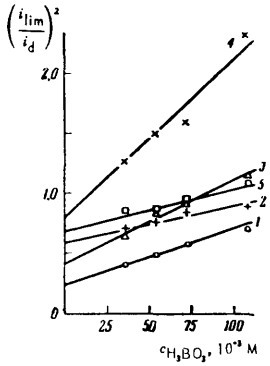

Fig. 3. Variation of $(i_{lim}/i_d)^2$ with concentration of undissociated H_3BO_3 in a borate buffer of pH 8.40 (ionic strength 0.5) for catalytic hydrogen waves produced by $\sim 0.5 \times 10^{-3}$ M solutions of: 1) pyridine; 2) 2-picoline; 3) 3-picoline; 4) 4-picoline; 5) 2,6-lutidine.

explained by postulating that the height of the wave is limited by a reaction which is of second order with respect to the catalyst.

Sometimes, as in the discharge of the anabasinium ion[50], bimolecular radical reactions of type (III) give rise to relatively stable HB–BH dimers as intermediates, which slowly decompose into two B species and evolve molecular hydrogen. The HB–BH dihydrodianabasine dimers become less stable at higher temperatures, and their formation (or, more precisely, their rate of decomposition) no longer affects the overall rate of process (III)[50].

B, the basic form of the catalyst produced by reaction (III), is again protonated by reaction (I), discharged by reaction (II), once again regenerated, etc., each cycle of reactions (I–III) converting two protons from DH^+ into molecular hydrogen by a catalytic electrochemical reaction. Thus each catalyst species can "reprocess" many species of the proton donor.

The catalytic hydrogen evolution current is determined by the rate of processes (I–III). Under limiting current conditions, when the rate of the electrochemical step (II) is high enough to discharge all BH^+ species present at the electrode surface, the height of the catalytic wave is determined by the rate of formation of BH^+ at the electrode. In most cases, this process is controlled by protonation of the basic form of the catalyst, a reaction whose overall rate constant, shown as ρ in scheme (I), is in reality the sum of the rate constants for all possible interactions between the catalyst and proton donors in solution:

$$\rho = k_1[DH^+]_1 + k_2[DH^+]_2 + \cdots + k_n[DH^+]_n. \qquad (1)$$

The equilibrium constant relating the basic and the acidic form of the catalyst, σ, is an important parameter of the catalytic system. As in other protolytic reactions, the value of σ is determined only by the acid dissociation constant of the protonated form of the catalyst and by the solution pH: unlike ρ, this constant is unaffected by the nature of the concentration of the buffer present in solution:

$$\sigma = \frac{[B]}{[BH^+]} = \frac{K_A}{[H^+]}. \qquad (2)$$

We shall now consider the relationship between the limiting catalytic current and solution composition which the suggested model of the catalytic wave predicts.

Consider first a process limited only by the rate of protonation (I), *i.e.* in which the rate of regeneration of the catalyst by reaction (III) is large enough. To simplify matters, we shall assume that the solution contains only one kind of proton donor:

$$\rho = k_{H^+}[H^+].$$

The further assumption, frequently justified in practice, is also made that the protolytic equilibrium lies on the side of the basic form of the catalyst, *i.e.* $\sigma > 1$, and that the rapid and complete regeneration of the catalyst produces a steady state, established very shortly after formation of the drop, in which the equilibrium concentrations of BH^+ and B are maintained even at relatively short distances from the electrode[51]. Under these conditions, the limiting catalytic current is given by the expression

$$i_{lim} = k_{H^+}[H^+]_s[B]_s s F a, \qquad (3)$$

where s denotes the mean area of the dropping electrode, F is the Faraday, and a is a proportionality factor equal to the thickness μ of the reaction layer if the catalyst were not adsorbed. For the so-called surface waves, discussed below, a is a factor which converts bulk concentrations into surface concentrations with allowance for catalyst adsorption. The subscript s indicates that the concentrations are to be taken close to the electrode surface.

In the catalytic cycle one hydrogen ion is consumed for every electron transferred. Hence the hydrogen ion concentration near the surface can be expressed, using the Ilkovič equation, as

$$[H^+]_s = [H^+]_0 - i_{lim}\kappa_{H^+}, \qquad (4)$$

where $[H^+]_0$ is the concentration of hydrogen ions in the bulk of the solution and κ_{H^+} the Ilkovič constant for hydrogen ions ($\kappa_{H^+} = i_d/[H^+]_0$).

The quantity $[B_S]$ is proportional to the catalyst concentration in solution c_{cat}, but if the catalyst is not adsorbed, and $\sigma \gg 1$, we may write $[B_S] = c_{cat}$. Thus, replacing $[B_S]$ by c_{cat} and inserting into Eqn. (3) the value of $[H^+]_S$ given by Eqn. (4), we find

$$i_{lim} = \frac{k_{H^+} s F a c_{cat}}{1 + k_{H^+} s F a c_{cat} \kappa_{H^+}}[H^+]_0. \qquad (5)$$

Eqn. (5) predicts, in agreement with experiment, a variation of catalytic limiting current with catalyst concentration of the same general form as the Langmuir adsorption isotherm: the reader can easily check that, as c_{cat} increases, the height of the catalytic wave tends towards a limit given by $\kappa_{H^+}[H^+]_0$, *i.e.* towards the diffusion current of hydrogen ions in the given solution.

The influence of the rate of reaction (III) on the height of the catalytic wave becomes appreciable at very low catalyst concentrations. Assuming that reaction (III) occurs only in the bulk reaction layer μ_d, in the limiting case, when the process is wholly determined by the rate of the

bimolecular reaction, the height of the catalytic wave can be expressed (after Brdička and Wiesner[52,53]) as

$$i_{lim} = sFk_d \mu_d [BH]_s^2, \quad (6)$$

where k_d is the rate constant of the bimolecular reaction (III). The thickness of the reaction layer μ_d is given[54], for a bimolecular reaction, by

$$\mu_d = \sqrt{D/k_d[BH]_s}, \quad (7)$$

whence

$$i_{lim} = sFk_d^{1/2} D^{1/2} [BH]_s^{3/2}, \quad (8)$$

where D is the diffusion coefficient of the catalyst.

Under conditions where the catalytic current is limited by the rate of the bimolecular reaction (III), $[BH]_s$ is proportional to c_{cat}, and Eqn. (8) requires that i_{lim} should vary with the 3/2 power of catalyst concentration. This behaviour is observed experimentally at very low values of c_{cat} (Fig. 2). The rate of process (III) increases rapidly with c_{cat}, and soon ceases to be the only rate-determining step. Under these conditions the limiting catalytic current departs from Eqn. (8).

The method of Brdička and Wiesner cannot give a general expression for the limiting catalytic current over a wide range of catalyst concentrations. Yet, it has been successfully applied[55] to particular catalytic hydrogen waves. Koutecký[51] has given a general solution of the problem, based on his so-called "exact" method, for the bulk chemical reactions (I) and (III) and the reversible electrochemical step (II).

The conclusions, and the experimental results, given above are only an illustration of the suggested mechanism of formation of the catalytic wave, and apply only to some of the simpler systems. In general, catalytic hydrogen evolution is a more complicated process, involving adsorbed catalyst species. It is powerfully affected by the structure of the electrical double layer at the electrode surface, and therefore also by the composition of the solution. Nevertheless, all the experimental data so far available on catalytic hydrogen evolution and the influence of various factors on this process can be satisfactorily explained on the basis of the suggested mechanism for the catalytic wave (*cf.* Mairanovskii *et al.*[56]).

II. BULK CATALYTIC HYDROGEN WAVES WITH A REVERSIBLE ELECTROCHEMICAL STEP IN BUFFERED SOLUTIONS

1. Reversible Catalytic Hydrogen Waves

Catalytic hydrogen waves in which the electrochemical step (II) is reversible were first observed[27,57] in pyridine solutions.

Reversibility of the electrochemical step during discharge of pyridinium ions was postulated[27] by analogy with the discharge of *N*-alkylpyridinium cations, which has repeatedly been shown[48,49,58] to be a reversible process, and later confirmed by the observation of a reaction pseudocapacity in impedance measurements[59] on a mercury electrode in pyridine solutions.

Electron transfer appears to proceed reversibly also in electrochemical processes involving other substances with an 'onium' structure, such as quaternary ammonium salts[60].

2. Bulk Nature of Catalytic Waves in Pyridine Solutions

When catalytic waves are limited by the rate of the preceding chemical reaction (I), the latter can occur either in the bulk of the solution adjacent to the electrode surface or at the surface itself, in which case adsorbed substances are involved. The waves can therefore be classified[31,61,62] into bulk, surface, and mixed waves, the third type referring to systems for which the bulk reaction and the surface reaction have comparable rates. The surface component of the kinetic current can become comparable with the bulk component at a surface coverage (by adsorbed catalyst in its electrochemically inactive form, B) as low as a few tenths of 1%. Since many of the compounds giving rise to catalytic hydrogen evolution are markedly surface-active, most catalytic waves are definitely of the surface type.

Waves in pyridine solutions are among the very few exceptions. Studies of their $i-t$ curves have shown, however, that catalytic pyridine waves associated exclusively with bulk effects can only be obtained[63,64] in the presence of a concentration of an indifferent electrolyte (greater than 0.2 *M* in the case of potassium salts[63]) high enough to inhibit the adsorption of pyridine. Very short drop times are also needed: they can be achieved by using a wiper to assist drop detachment.

3. Equations for Reversible Bulk Catalytic Hydrogen Waves in Buffered Solutions

We shall now apply the concept of a reaction layer to the commonest type of catalytic wave, in which the limiting current is determined only by the rate of the preliminary protonation reaction (I), and the rate of the subsequent bimolecular reaction (III) has no effect. If the preliminary reaction (I) takes place in the bulk, the thickness of the reaction layer is given by

$$\mu = \sqrt{D/\rho\sigma}, \quad (9)$$

where D is the appropriate diffusion coefficient.

The height of the catalytic wave is determined by the number of BH^+ species appearing per unit time in a layer of thickness μ:

$$i_{lim} = sF\mu [B]_s \rho. \quad (10)$$

Making the frequently justified assumption that $\sigma \gg 1$, *i. e.* that the catalyst exists in solution mainly in its basic, unprotonated form, and that complete catalyst regeneration can rapidly set up a steady state at the electrode, we equate $[B]_s$ to the total analytical concentration of catalyst in solution c_{cat}. Using Eqn. (9), we obtain

$$i_{lim} = sFc_{cat} D^{1/2} \rho^{1/2} / \sigma^{1/2}. \quad (11)$$

We now write an Ilkovič equation for the hypothetical difffusion current corresponding to normal, diffusion-limited discharge of the catalyst with $n = 1$:

$$i_d = 1.235\, sFc_{cat} D^{1/2} t^{1/2}, \quad (12)$$

where t is the drop time of the electrode. Then[55]

$$\frac{i_{lim}}{i_d} = 0.81 \sqrt{\frac{\rho t}{\sigma}}. \quad (13)$$

Eqn. (13) readily leads, on the basis of experimental values of i_{lim}, to the overall rate constant ρ for the protonation reaction, defined by Eqn. (1). An expression almost identical to Eqn. (13) has also been derived by an exact solution

of the depolarisation problem under the present set of conditions [*cf.* Eqn. (49) of Koutecký *et al.* [51]].

If the limiting current of the catalytic wave is significantly affected also by the rate of the subsequent reaction, the exact solution[51] gives the following expression for ρ:

$$\rho = \frac{(i_{lim}/i_d)^2 \sigma}{0.81^2 t \left\{1 - \left[\frac{3}{2} \times \frac{(i_{lim}/i_d)^2}{0.81^2 k_d c_{cat} t}\right]^{1/4}\right\}^2} \quad (14)$$

This expression tends towards Eqn. (13) as the rate of the bimolecular interaction of the electrode products increases, *i.e.* when c_{cat} or k_d increases. An expression similar to Eqn. (14) can also be deduced from the reaction layer concept [Eqn. (30) of Hanuš *et al.* [55]: this differs from Eqn. (14) only by the numerical coefficient 3/2 within the square bracket.

When the limiting catalytic current is determined by the bimolecular step (III), the exact solution of the depolarisation problem gives an expression for the limiting current [Eqn. (50) of Ref. 51] differing from Eqn. (8) only by a numerical factor of $\sqrt{2/3}$. Thus, the depolarisation problem for catalytic waves of this type can be solved by an exact and by an approximate method, with practically identical results.

The equation for the shape of a reversible, bulk catalytic hydrogen wave, under conditions of rate limitation by the preliminary protonation reaction and with $\sigma \gg 1$, can be derived[27,55] by introducing the values of $[BH^+]_s$ and $[BH]_s$ [*i.e.* the surface concentrations of the components of the redox system (II)] into the Nernst equation:

$$E = e_0 - \frac{RT}{F} \ln \frac{i^{1/3}}{i_{lim} - i}, \quad (15)$$

The characteristic potential ϵ_0, independent of catalyst concentration, corresponds to the point on the wave at which $i^{2/3} = i_{lim} - i$, and is given by

$$e_0 = E_0 - \frac{RT}{3F} \ln \left(\frac{sFD^{1/3} \rho^{1/3} \sigma^{1/3}}{k_d} \right), \quad (16)$$

where E_0 is the redox potential of system (II).

The exact solution of the depolarisation problem[51] gives the following expression for the half-wave potential in the present case:

$$E_{1/2} = E_0 + \frac{RT}{3F} \ln \frac{c_{cat} k_d}{3z^2 \rho}. \quad (17)$$

However, a similar expression for $E_{1/2}$ can also be obtained[27,55] from Eqn. (15), putting $i = \frac{1}{2} i_{lim}$.

4. Experimental Test of the Equations for Reversible Bulk Waves in Buffered Media

The sharpest catalytic waves produced by pyridine and its homologues are observed[26,27,63,65] in borate and veronal buffer solutions (pH 7.5–10). Under these conditions the limiting catalytic current, as required by theory, is proportional to the area of the dropping electrode and independent of the height of the mercury column. The limiting step is protonation of the catalyst. Thus, an increase in the buffer capacity of the solution at constant pH and ionic strength must raise the limiting catalytic current (Fig. 3), since it increases the rate of protonation ρ. Increase in pH, *i.e.* in $\sigma = K_A/[H^+]$, has been found by many experimenters[27,56,65,66] to depress the catalytic wave [see Eqn. (11) or (13)].

In accordance with Eqn. (15), bulk catalytic hydrogen waves with a reversible electrochemical step are found to be asymmetrical. When plotted as E against $\log i^{2/3}/(i_{lim} - i)$, they give straight lines[27] with a reciprocal slope of ~ 59 mV. The $E_{1/2}$ values [see Eqn. (17)] are shifted[27] by about 20 mV in the positive direction by a tenfold increase in c_{cat}.

The half-wave potential of a reversible bulk wave becomes more negative at higher pH values, *i.e.* on increasing σ. As required by theory [see Eqn. (17)], $\Delta E_{1/2}/\Delta pH \simeq$ $\simeq$ -40 mV provided the pH is not too high (Fig. 4). At pH > 8.8, $E_{1/2}$ begins to increase more slowly with σ: this effect, which is associated with the structure of the double layer, is discussed in detail in the following sections.

The influence of the buffer capacity of the solution on the $E_{1/2}$ value of a reversible wave is the most revealing test of the suggested mechanism of the appearance of catalytic waves. A shift in $E_{1/2}$ towards less cathodic potentials is expected, for an increase in buffer capacity, in most systems where the rate is limited by preliminary protonation. This effect has been observed, for example, in the reduction of nitro-compounds in acidic media[67]. The theory of catalytic waves developed by Knobloch[14] and by von Stackelberg and Nürnberg[19] also requires a positive shift in $E_{1/2}$ with increase in buffer capacity. However, and in qualitative agreement with Eqn. (17), Fig. 5 shows that the $E_{1/2}$ value of reversible catalytic waves becomes about 20 mV more negative for a tenfold increase in ρ (*i.e.* when the buffer capacity of the solution is increased).

When pyridine is used as a catalyst, a clearly defined limiting catalytic current due to the bimolecular reaction (III) cannot be obtained[26]. This practical complication arises from the formation, below pH 7.0, of appreciable quantities of a catalytically active pyridine polymer[64]. Nevertheless, the catalytic pyridine wave has been studied down to pH 6.0 (acetate buffer), and it has been shown that under these conditions the current is mainly limited by the bimolecular reaction[26,66]. An approximate value for the rate constant of this reaction has also been obtained (5×10^8 litre mole^{-1} sec^{-1} at 25°).

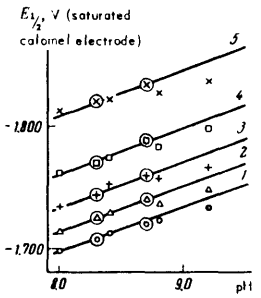

Fig. 4. Variation of $E_{1/2}$ of the catalytic wave with solution pH at catalyst concentration ~0.5×10^{-3} M and $\rho \simeq 1500$ sec^{-1}. Catalyst: 1) pyridine; 2) 3-picoline; 3) 2-picoline; 4) 2,6-lutidine; 5) 4-picoline. Single points — borate buffer solutions; circled points — veronal solutions.

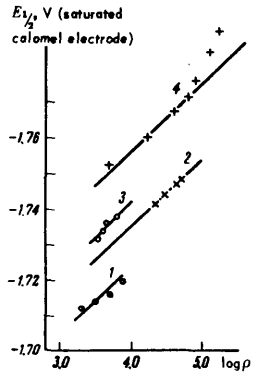

Fig. 5. Variation of $E_{1/2}$ of the catalytic wave in pyridine solutions with measured value of ρ: 1) veronal buffer, pH 8.3; 3) borate buffer, pH 9.0; 2) and 4) ammoniacal solutions of pH 9.0 and 9.5.

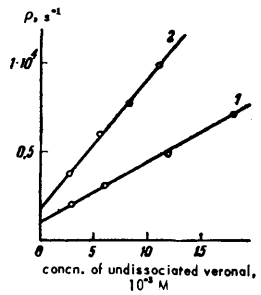

Fig. 6. Variation of ρ with concentration of undissociated veronal: 1) pH 8.30; 2) pH 8.70.

Limitation of a reversible catalytic wave by the rate of bimolecular regeneration can be demonstrated rather more clearly by using[26] the waves of 2,6-lutidine.

5. Evaluation of the Rate Constants for Catalyst Protonation. Influence of Double Layer Structure on Protonation in the Bulk Reaction Specie.

The value of ρ — the rate constant for catalyst protonation in the given solution — can be calculated from the limiting current of bulk catalytic waves by applying Eqn. (14). The hypothetical diffusion current i_d of the catalyst is calculated from the Ilkovič equation (assuming $n = 1$) or assumed equal to the diffusion current for the discharge of a compound having similar structure.

The value $k_d = 5 \times 10^8$ litre mole^{-1} sec^{-1} has been adopted[56,66] in calculations relating to pyridine waves. Its precision is quite low, but since the expression in braces in the denominator of Eqn. (14) is very close to unity, even large fluctuations in the value of k_d have little effect on the value of ρ.

The individual rate constants for catalyst protonation by different acids can be derived from the variation of ρ with the concentration of the appropriate proton donor, keeping the concentration of any other proton donors constant. Fig. 6, for example, shows the variation of ρ with the concentration of undissociated veronal, one of the components of the buffer mixture, at constant pH and ionic strength. The slope of the linear plots of ρ against the concentration of the acid component gives directly the rate constant for catalyst protonation under the influence of this particular proton donor. The individual rate constants for catalyst protonation determined in this way are found to increase with pH. The observed increase in rate constant is only apparent, however, and arises from the increasing effect of double layer structure at high solution pH[56].

The structure of the electrical double layer has an effect on the distribution of ions and on the rate of their migration in the layer of solution adjacent to the electrode[68-70]. Grabowski and Bartel[71] were the first to consider the influence of double layer structure on the preliminary protonation reaction, but the problem was later discussed in a more general way by a number of other workers[72-74].

If the reaction layer is much thicker than the diffuse part of the double layer, the effect of the double layer on the mean ionic concentrations within the reaction layer can be neglected. As the reaction layer shrinks, an increasing fraction of its thickness is occupied by the diffuse part of the double layer, and the influence of the double layer becomes more significant. With bulk catalytic currents the thickness of the reaction region decreases when the pH increases [*i.e.* when σ increases, see Eqn. (9)], and the effect of double layer structure becomes correspondingly greater. It has been shown[31,62,75] that the effect of the field surrounding the electrode is to lower the pH of the solution close to the cathode well below its bulk value. This explains the apparent increase in rate constant upon decreasing the thickness of the reaction layer.

On varying the solution pH at constant ionic strength, only the thickness μ of the reaction layer is altered, the effective thickness of the diffuse part of the double layer remaining constant. The relative thickness of the two layers can also be varied by altering only the thickness of the diffuse part of the double layer whilst keeping μ constant: this is done by varying the ionic strength of the solution at constant pH and buffer capacity. Calculation shows that the decrease in height of the catalytic pyridine wave observed[31] on increasing the ionic strength of the solution corresponds exactly to the change in the effect of double layer structure[76].

To find the true rate constants for catalyst protonation, free from errors due to electrode field effects, the experimentally observed values must be extrapolated to the region of very high μ, *i.e.* very low pH, where the effect of double layer structure is undetectable. The experimental, "apparent" values of individual protonation constants $k'_A = \Delta\rho/\Delta[DH^+]_A$ are found, by plots such as those of Fig. 6, to vary linearly with the reciprocal of hydrogen ion concentration[56,65,66]. The true protonation rate constants k_A are found by plotting k'_A against $1/[H^+]$ and extrapolating to $1/[H^+] \to 0$, as in Fig. 7 (taken from Ref. 56). The intercepts of the straight lines on the vertical axis gave the following true rate constants for pyridine[56,66]: $k_{H_3BO_3} = 9.0 \times 10^3$ and $k_{veronal} = 1.2 \times 10^5$ litre mole^{-1} sec^{-1}.

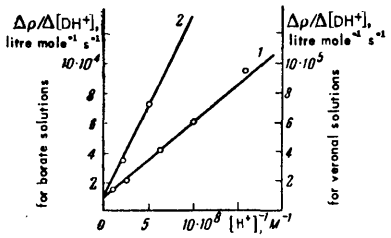

Fig. 7. Effect of $1/[H^+]$ on the observed individual rate constants for the reaction of pyridine with H_3BO_3 (curve 1) and veronal (curve 2).

The y-intercepts of linear plots of the type shown in Fig. 6 give the "apparent" values ρ_0', *i.e.* the sum of the rate constants for protonation under the influence of water and of hydrogen ions. To find the true ρ_0 values, free from errors due to double layer effects, ρ_0' must be divided by the ratio k_A'/k_A for the given solution. The rate constants for the protonation of pyridine by hydrogen ions ($k_{H^+} \simeq 2.5 \times 10^{10}$ litre mole^{-1} sec^{-1}) and by water ($k_{H_2O} \simeq$ $\simeq$ 7 litre mole^{-1} sec^{-1}) have been evaluated[56] from the variation of the corrected ρ_0 values with $[H^+]$.

The rate constant for the protonation of pyridine by different donors increases with the acid strength of the proton donors. As with other protolytic reactions, the individual protonation rate constants of pyridine are related to the dissocation constants of the acids K_A by the Brønsted expression (see, for example, Ref. 77)

$$k_A = p\,Q\left(\frac{q}{p}K_A\right)^{\alpha}; \qquad (18)$$

where Q and α are constants, and p and q are the so-called static factors, giving respectively the number of protons which can be removed from different atoms of the given acid or added to different atoms of its conjugate base. The value of α for the protonation of pyridine at 25° in a solution of ionic strength 0.5 has been found[66] to be 0.58

6. Effect of Temperature on Bulk Catalytic Waves in Buffered Solutions

The height of bulk catalytic hydrogen waves increases with temperature. The individual rate constants for the protonation of pyridine were evaluated[66], at various temperatures, from the variation of the limiting current with concentration of the acid component, and corrected for the effect of the double layer. When plotted against the reciprocal of temperature, these data afforded[66] the activation energies for the reactions between pyridine and boric acid (5.1 kcal mole^{-1}), veronal (6.4 kcal mole^{-1}), hydronium ions ($\sim$ 2.4 kcal mole^{-1}), and water ($\sim$ 6 kcal mole^{-1}).

The linear Brønsted plots [Eqn. (18)] for the protonation of pyridine, at different temperatures, all have the same slope, within experimental error, and are only slightly displaced parallel to one another[66].

7. Effect of Stirring on Catalytic Hydrogen Waves under Conditions of Polarographic Maxima of the Second Kind

The turbulence caused by the tangential motion of the surface of a dropping mercury electrode at relatively high drop rates can distort the diffusion layer, leading to an increase in the observed polarographic diffusion current. This phenomenon has been studied in detail by Frumkin and his coworkers[68], and has been termed a polarographic maximum of the second kind[78,79].

Stirring, under conditions of a maximum of the second kind, often increases the catalytic current[80] of bulk catalytic waves in pyridine solutions. The effect of stirring depends on the thickness of the reaction layer μ, reaching a maximum of almost twice the diffusion current at $\mu \simeq 100$ Å. Stirring effects are absent when the rate-limiting reaction occurs in a very thin layer (< 20 Å) or at the electrode surface itself (adsorbed reactants). In these circumstances the reaction layer is entirely within the interfacial layer of solution, which does not move with respect to the electrode.

III. REVERSIBLE BULK CATALYTIC HYDROGEN WAVES IN UNBUFFERED SOLUTIONS

In a neutral or alkaline unbuffered solution water is practically the only proton donor DH^+, with hydroxide ions as the conjugate base D, so that

$$p = k_1[H_2O] \text{ and } p\sigma = k_2[OH^-]_s. \qquad (19)$$

It follows from our mechanism of the process that each catalytic cycle of reactions (I–III) produces one OH^- ion. Using the Ilkovič equation to calculate their rate of removal from the electrode, and noting that $[OH^-]_S \gg [OH^-]_0$ when neutral or weakly alkaline solutions are electrolysed, we find

$$[OH^-]_s = i/\kappa_{OH^-}, \qquad (20)$$

where κ_{OH} is the Ilkovič constant for OH^- ions. The thickness of the reaction layer for the protolytic reaction (I) is determined, in this case, by the rate at which hydroxide ions can react with the active form of the catalyst BH^+. Hence, if μ is so small that the concentration of OH^- can be assumed constant throughout the reaction layer, the following expression for μ will apply:

$$\mu = (D/k_2[OH^-]_s)^{1/3} = (D\kappa_{OH^-}/k_2 i)^{1/3}, \qquad (21)$$

where D is the diffusion coefficient of the catalyst.

The limiting current can be found[57] by combining Eqns. (10) and (21) with Eqn. (19), and noting that $[B]_S = c_{cat}$:

$$i_{lim} = (Qc_{cat})^{2/3}, \qquad (22)$$

where

$$Q = k_1 sF[H_2O]D^{1/3}\kappa_{OH^-}^{1/3}/k_2^{1/3}. \qquad (23)$$

We see from Eqn. (22) that in unbuffered solutions the height of the catalytic wave should vary with the 2/3 power of catalyst concentration: this agrees well with experiment[63] (see Fig. 8).

An equation for the wave can be obtained by introducing the values of $[BH^+]$ and $[B]_S$ into the Nernst equation:

$$E = e_0^* - \frac{RT}{F}\ln\frac{i^{2/3}}{i_{lim}^{2/3} - i^{2/3}}, \qquad (24)$$

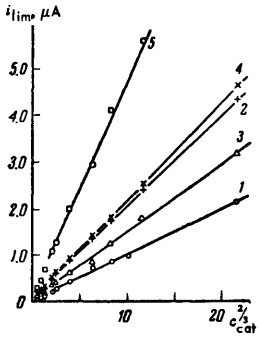

Fig. 8. Variation of limiting catalytic current with the 2/3 power of catalyst concentration (in 10^{-3} mole litre^{-1}) for waves in unbuffered solutions: 1) pyridine; 2) 2-picoline; 3) 3-picoline; 4) 4-picoline; 5) 2,6-lutidine.

which can be rewritten in the form

$$e_0^{\cdot} = E_0 + \frac{RT}{F} \ln \frac{k_d^{1/6} K_{OH^-}^{1/3}}{k_s^{1/6} (SF)^{1/6} D^{1/6}} + 59 \text{ mV}, \qquad (25)$$

if the current in Eqn. (24) is expressed in μA.

Fig. 9 shows the variation of the function

$$\log \frac{i^{3/2}}{i_{lim}^{3/2} - i^{3/2}},$$

with potential for catalytic waves produced at catalyst concentrations of the order of 2.4×10^{-2} M (the results for pyridine waves are reported at several values of c_{cat}). The upper part of the polarograms (above some current value which overcomes the small but finite buffer capacity of the KCl solutions due to traces of dissolved CO_2 and other impurities) is satisfactorily described by Eqn. (24), as

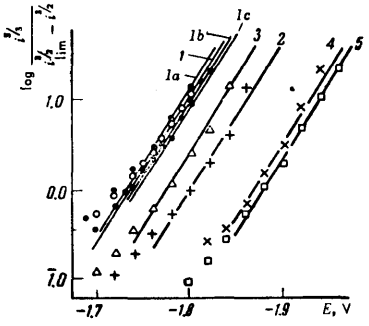

Fig. 9. Variation of $\log i^{5/3}/(i_{lim}^{3/2} - i^{3/2})$ with E for catalytic hydrogen waves with a base electrolyte of 0.5 M KCl in 24×10^{-3} M solutions of: 1) pyridine; 2) 2-picoline; 3) 3-picoline; 4) 4-picoline; 5) 2,6-lutidine. Curves 1*a*, 1*b*, and 1*c* correspond to pyridine concentrations of 16, 40, and 100 10^{-3} M.

shown by the fit of the experimental points on the straight lines calculated from this equation (Fig. 9). The function of current which appears in Eqn. (24) should be described by a single straight line, irrespective of catalyst concentration, for waves produced by a given catalyst. However, the results for different concentrations of pyridine (Fig. 9) show a slight shift towards negative potentials with increasing pyridine concentration. This may be due to an increase in pH in the bulk of the solution, caused by increasing the catalyst concentration, of which no account was taken in deriving the equations.

IV. SURFACE CATALYTIC HYDROGEN WAVES

1. Fundamental Relations

In catalytic waves purely of the "surface" type the catalyst undergoes the protonation reaction at the electrode surface whilst in the adsorbed state[61,81,82].

The surface catalytic current is proportional to the amount of catalyst adsorbed. Hence we can write, from the general mechanism of formation of catalytic waves limited by the rate of protonation,

$$i = sF(\rho_{surf}\Gamma - \rho_{surf}{}^{o}\Gamma'), \qquad (26)$$

whilst the limiting current is given by

$$i_{lim} = sF\rho_{surf}\Gamma, \qquad (27)$$

where Γ and Γ' are the amounts of adsorbed base (B) and acid (BH^+) respectively. Surface catalytic currents are found in practice[83] to have an irreversible electrochemical step. Therefore, the current should be calculable from the following formula, taken from the slow-discharge theory[68]:

$$i = sk_{el}\Gamma' e^{-\frac{\alpha FE}{RT}}. \qquad (28)$$

If the adsorption of the catalyst were independent of electrode potential, and equal to the value Γ^0 which corresponds to the potential of maximum adsorption E_{max}, the catalytic wave would be described [on the basis of Eqns. (26)–(28)] by the expression

$$E = E_{1/2} - \frac{RT}{\alpha F} \ln \frac{i^0}{i_{lim}^0 - i^0}, \qquad (29)$$

where the superscript zero denotes adsorption at E_{max}.

We shall suppose that the adsorption of the catalyst obeys the Langmuir isotherm

$$\Gamma_e = \Gamma_\infty \frac{\beta c_{cat}}{1 + \beta c_{cat}}, \qquad (30)$$

where Γ_e and Γ_∞ are the equilibrium and the maximum adsorption respectively, and β is the adsorption index. Adsorption equilibrium is not usually established during the lifetime of a drop[84], and we must write, for time t after the onset of drop formation,

$$\Gamma = y\Gamma_e. \qquad (31)$$

The extent of approach towards equilibrium (y) depends on the adsorption time, on the rate of supply of material to the electrode, and on the value of β.[84,85] Far from equilibrium, *i.e.* when $y \ll 1$, y varies approximately with the square root of the adsorption time[85]:

$$y \simeq kt^{1/2}. \qquad (32)$$

Using the results of an accurate calculation[84] on the rate of diffusion-limited adsorption on a dropping electrode, it can be shown (as in Fig. 10) that at constant c_{cat} and t the quantity y increases with β according to the equation[81]

$$y = 1 + \beta c_{cat} \quad (y \leqslant 0.55). \tag{33}$$

According to Frumkin[86], adsorption at an electrode decreases in the following manner as the potential changes from that for maximum adsorption:

$$\beta = \beta^0 e^{-\frac{1/_2(C-C')}{RT\Gamma_\infty}\varphi^0} = \beta^0 e^{-a\varphi^0}. \tag{34}$$

where φ is the potential relative to E_{max} (*i.e.* $\varphi = E - E_{max}$), C and C' are the values of the double layer capacity of the electrode at zero coverage and at full coverage of the electrode by the surface-active substance.

Gouy and Butler, working with organic bases in neutral and in acid solutions, [87-89] have shown that the basic form of the catalyst has a significantly higher surface activity on mercury than the acidic form. Furthermore, the adsorbability at the cathode of the cationic form varies much less with potential than does that of the uncharged basic form[87]. Thus, the change in adsorption of the catalyst is largely determined by the change in adsorption of the basic form, particularly when equilibrium (I) lies far over to the left, even though the extent of adsorption depends also on the relative amounts of the two forms (*i.e.* on the pH).

Because of the decrease in adsorbability of the catalyst at more cathodic potentials, the observed catalytic current is smaller than i^0: $i/i^0 = \Gamma/\Gamma^0$, or, using Eqns. (30) and (31),

$$\frac{i}{i^0} = \frac{\mu\beta}{1+\beta c_{cat}} : \frac{\mu^0\beta^0}{1+\beta^0 c_{cat}}. \tag{35}$$

Introducing Eqns. (33) and (34), and confining ourselves to values of $y < 0.55$ (a condition nearly always satisfied at a dropping electrode in normal circumstances), we find

$$\frac{i}{i^0} = \frac{\beta}{\beta^0} = e^{-a\varphi^0}. \tag{36}$$

The characteristic, humpbacked curves given by surface catalytic hydrogen waves[81] can be described by combining Eqns. (29) and (36). The appearance of the hump on surface waves is illustrated in Fig. 11: the maximum

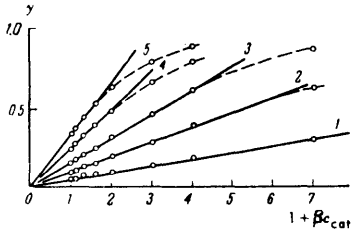

Fig. 10. Variation of y with $1 + \beta c_{cat}$ for different adsorption times on a dropping electrode (after Delahay and Fike[84]):
1) 0.2; 2) 0.5; 3) 1.0; 4) 2.0; 5) 4.0 s.

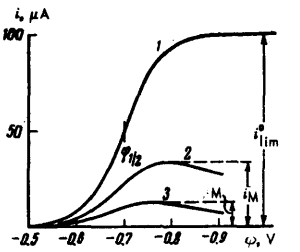

Fig. 11. Demonstration of the formation of humpbacked surface catalytic waves:
1) no allowance for change in adsorption with potential, Eqn. (29); 2) and 3) change in adsorption allowed for by putting a = 1.63 V^{-2} and a = = 3.27 V^{-2}, respectively, in Eqn. (36).

height i_M of the wave differs from the limiting current, but since i_M is, in most cases, proportional to i^0_{lim}, the former quantity, which is directly measurable, can be used for analytical purposes.

2. Experimental Test of the Equations for Surface Waves

The correctness of the above equations has been demonstrated[81] for the concrete case of the surface catalytic waves produced by anabasine and by quinine.

The surface catalytic wave, like all waves in which the rate of preliminary protonation is rate-determining, increases with the buffer capacity of the solution. The variation of the catalytic current in anabasine solutions with the concentration of undissociated acetic acid has been used[81] to calculate the rate constant for protonation of adsorbed anabasine under the influence of CH_3COOH: the value obtained was 2.9×10^5 litre $mole^{-1}$ sec^{-1} at a potential of -1.84 V relative to the saturated calomel electrode.

Polarisation of the adsorbed species by the electric field surrounding the electrode probably can affect[71] the rate constants for surface reactions.

Surface waves often show an interesting and unusual variation with h, the height of the mercury column above the dropping electrode. Whereas the limiting diffusion currents and the heights of the preliminary adsorption waves decrease with decrease in h, whilst bulk kinetic and catalytic currents are independent of h, it is frequently found[31] that waves limited by preliminary surface reactions increase as h decreases. This phenomenon is observed when adsorption equilibrium is not reached: under these conditions longer drop times (*i.e.* adsorption times) enable adsorption equilibrium to be approached more closely, and therefore raise the value of Γ.

The surface component of the kinetic current density often varies with time as required by Eqn. (32). This was demonstrated by analysing the second wave of the polarograms of maleic acid[90]. Vojíř[91,92] has reported an increase in the catalytic waves upon lowering the mercury reservoir.

Other workers[93,94] have observed similar effects for currents due to complexes of cobalt with amino-acids and proteins. Von Stackelberg and Fassbender[17] plotted $i-t$ curves during the lifetime of a single drop, and showed that the catalytic current is given by the approximate relation $i \simeq t^{\nu}$, where the value of ν is greater than unity in the presence of a high-molecular-weight catalyst. Inspection of their Fig. 2 suggests that ν can reach the value of $\sim 7/6$, which is accounted for by the combined effects of increase in electrode area (2/3) and increase in the amount of catalyst adsorbed [1/2, see Eqn. (32)].

Surface catalytic waves, like surface kinetic waves[90], are often practically unaffected by changes in temperature[50], since an increase in the protonation rate constant of the catalyst can be compensated by decreased adsorption of the catalyst on the electrode surface[31].

It is well known that addition of surface active compounds (SAC) to the polarographic solution can often cause a drastic decrease in the catalytic wave (see, for example, Knobloch[15] and Mairanovskii[61]). The effect is due to displacement of the catalyst from the electrode surface by the added SAC. The extent to which the SAC suppresses the catalytic wave depends, as expected, on the ratio of the SAC and catalyst concentrations and on their relative adsorbabilities.

If desorption of the SAC occurs before that of the catalyst and the desorption potential of the SAC is in the range of catalytic hydrogen evolution, the polarograms show a sharp increase in catalytic current coinciding with desorption of the SAC[95,96], which can be mistaken for a new wave. This is reminiscent of the formation of spurious reduction waves upon desorption of an SAC able to inhibit the electrode process[97] or to suppress the tangential flow of the mercury.

3. Mixed Bulk and Surface Catalytic Waves

All catalytic currents observed in practice must be the sum of a surface term and a bulk term: systems in which either of the two components can be neglected are extremely rare.

The surface component of the current increases as the ionic strength of the solution decreases[98] and becomes predominant in solutions containing only non-adsorbable cations[99,100] such as lithium ions[101].

The bulk and the surface components of the current usually give one common wave on the polarogram, even when two separate waves could have been expected. The large increase in concentration (at the electrode) of irreversibly discharged species, resulting from adsorption of these species, sometimes gives rise[102,103] to additional polarographic waves corresponding to discharge of the strongly adsorbed species. The non-adsorbed species (or, more accurately, those whose adsorption is weaker or energetically less favourable) are discharged at more negative potentials. Thus, the surface catalytic wave should be shifted towards potentials less cathodic than that of the bulk wave by the sharp increase in catalyst concentration near the electrode accompanying the flow of surface currents. On the other hand, the mode of adsorption of the electrochemically active species (its orientation on the electrode surface, for instance) can influence the rate constant of the purely electrochemical step. Thus, in the polarography of indoleninium salts[104], whose discharge mechanism is in many ways analogous to the transfer of an electron to a protonated catalyst species, the slope of the wave suggests that the irreversibility of the process increases with pH. This can be ascribed to more ready adsorption of the depolariser when in its basic, uncharged form. We may conclude, therefore, that adsorption can significantly alter the rate of the electrode process, and shift the half-wave potential both in the anodic and in the cathodic direction.

Bulk waves in solutions of pyridine and its homologues have a reversible electrochemical step: with surface catalytic waves, on the other hand, no reversible electrochemical process has so far been reported. It is interesting to note, however, that a reversible catalytic hydrogen wave has been obtained[83] by adding a high concentration of a strongly adsorbable compound to quinine solutions. This decreased the total height of the wave approximately 30-fold and made the half-wave potential slightly more positive than $E_{1/2}$ for a surface wave of comparable height. This suggests that the bulk component of the catalytic wave observed in quinine solutions is reversible, and can be detected at potentials less negative than those of the surface wave. It should be possible, therefore, under favourable conditions, to resolve the combined catalytic wave into a bulk and a surface step: the resolution has been achieved with catalytic currents in quinine solutions[61].

The double "hump" observed by von Stackelberg *et al.*[18] on catalytic waves obtained in solutions of the leuco form of Malachite Green and of β-naphthoquinoline may also indicate separation of the current into a bulk and a surface term.

4. Effect of Double Layer Structure on Surface Catalytic Waves

In systems showing surface catalytic hydrogen waves, changes in the structure of the double layer have an effect on the adsorbability of the catalyst, on the pH of the layer of solution adjacent to the electrode, and also (to some extent) on the dissociation constant of adsorbed catalysts. For example, the maximum height of the catalytic wave decreases almost by a factor of three[75], and the potential at the maximum becomes more positive as a result of the increase in double layer capacity [and therefore also in the value of a, Eqn. (36)], following an increase from 0.04 to 0.08 M in the total concentration of sodium ions at constant pH, buffer capacity, and catalyst (quinine) concentration.

The catalytic wave is greatly decreased by changing from solutions containing Li^+ to solutions containing Cs^+ salts[75]. The effects observed on exploring the sequence $Li^+ \rightarrow Cs^+$ include an increase in the superequivalent adsorption of cations at the mercury electrode[99,100], a decrease in the absolute value of the ψ_1 potential, and an increase in the capacity of the double layer [and therefore also in the value of a in Frumkin's Eqn. (34)].

The difference in pH between the bulk of the solution and the layer of solution adjacent to the electrode is a simple function of the ψ_1 potential only in the case of surface waves with preliminary protonation[31,62]. Thus it has been possible, in these systems, to make an almost quantitative allowance for the effect of changes in the concentration of potassium and sodium ions in solution on surface catalytic currents[75].

Some interesting observations by Pungor and Farsang[106-109] have also been explained[105] in terms of the effect of double layer structure. These workers reported that

the catalytic wave of quinine increases at first, and then decreases, when a tetraethylammonium salt is gradually added to the polarographic solution. Pungor and Farsang used phosphate buffer media, where the anions HPO_4^{2-} and $H_2PO_4^-$ are the main proton donors. Hence, low concentrations of the surface-active tetraethylammonium cation make the ψ_1 potential less negative and assist the approach of proton donors (phosphate anions) to the electrode. At higher concentrations, however, tetraethylammonium begins to displace the quinine from the electrode surface and lowers the catalytic current. Surface-active cations have a very similar effect on the surface recombination wave of anions[82,110,111].

5. Effect of Organic Solvents

Addition of organic solvents to catalytically active solutions lowers the catalytic currents[15,16,112-115].

Organic solvents, by suppressing the dissociation of proton-donor acids, raise the pH of the solution[116,117], lower the dissociation constant of the catalyst[112,116], and therefore cause σ to increase more relative to the change in pH. They also decrease the adsorbability of the catalyst very significantly — a very important effect with surface waves.

V. CATALYTIC WAVES DUE TO SULPHUR COMPOUNDS

1. Mechanism of the Process

Many organic compounds containing mercapto-groups show a marked tendency to give catalytic hydrogen waves, particularly in the presence of cobalt or nickel salts. Despite the many studies of catalytic waves in solutions of sulphur compounds (see, for example, the review articles listed in Refs. 5, 8, 9, 10, and the more recent experimental work[18,94-96,118-125]), some aspects of the mechanism of this process are still far from clear.

Brdička suggested[9,22] that hydrogen, being very mobile in the SH group, can be easily split off by the electrochemical reaction

$$RSH + e^- \rightarrow RS^- + H, \qquad (IV)$$

the resulting RS^- anions undergoing rapid protonation by the proton donors present in solution to regenerate the electrochemically active form RSH. A convincing argument in favour of this scheme was supplied by Brdička himself[9,126], who showed that the catalytic activity of thiols can be suppressed by adding salts of iodoacetic acid to the solution, the acid residue attaching itself to the sulphur in place of the labile hydrogen atom.

Mairanovskii and Neiman[127] found, in their study of the reduction of sulphones at a dropping electrode, that the reduction product (by a four-electron reaction) of *pp'*-dichlorodiphenylsulphone — probably *pp'*-dichlorodiphenyl sulphide — gives a catalytic wave despite the absence of an SH group. The authors conclude[127] that the catalytic wave of a sulphur-containing catalyst is formed by the same mechanism as the wave of a nitrogeneous base: the species undergoing discharge is a sulphonium ion, formed by protonation of the sulphide. Catalytic hydrogen evolution has been repeatedly observed with compounds containing sulphur as disubstituted sulphide (*e.g.* in solutions of ethylenebisthioglycollic acid[18] $HOOCCH_2SCH_2CH_2SCH_2COOH$ and also with the sulphides produced by two-electron electrolytic reduction of trisubstituted sulphonium ions[45]). The mechanism involving discharge of a sulphonium cation seems the more likely (see Frumkin and Andreeva[28]) from the point of view of electrical double layer effects. Considerations of double layer structure can also explain the suppression of catalytic activity resulting from interaction between the catalyst and iodoacetate ions: the product, being negatively charged, is prevented from reacting at the cathode.

The catalytic activity of cysteine is largely retained when its thiol hydrogen is replaced by a mercuribenzoate residue[21]:

$$RSH + ClHgC_6H_4COOH \rightarrow RSHgC_6H_4COOH.$$

This observation supports the sulphonium mechanism for the catalytic wave.

The available experimental data, however, do not justify a final choice between the two mechanisms for the catalysis of the hydrogen discharge process by substances containing mercapto-groups.

The reduction wave of Co^{2+} occurs below the potential of catalysed hydrogen evolution in solutions of sulphur compounds. This has led some workers to suggest[9,12] that the catalytically active centres are formed by adsorption of the organic catalyst on metallic cobalt, deposited on the mercury surface. Březina[128] refuted this view by showing that preliminary electrolysis of the solution with a static mercury cathode at a potential sufficient to discharge Co^{2+} does not give rise to catalytic hydrogen evolution: the accumulation of metallic cobalt in the electrode had no effect on subsequently measured polarographic waves. Hence, the catalyst is a complex involving cobalt ions and the organic compound.

We may assume that cobalt ions can form several complexes, of different composition[9], with any given thiol. Some of these will be so stable as not to participate in the electrochemical cobalt deposition reaction and will only take part in the catalytic hydrogen evolution. Stable Co^{2+} complexes, not decomposed at the cathode, are formed[129] by ethylenediaminetetraacetic acid, for example. Sunahara's report[121] that the height of the Co^{2+} discharge wave is decreased by adding cysteine to the solution also tends to confirm the formation, to some extent, of a complex between Co^{2+} and cysteine, which cannot be discharged with deposition of metallic cobalt.

Nevertheless, some metal ion discharge from the thiol complex must occur together with the catalytic evolution of hydrogen. This effect becomes noticeable at relatively low concentrations of the complex-forming ion. The shortage of these ions in the neighbourhood of the electrode, aggravated by their partial discharge, can give rise to a situation in which the catalytic current is a function of the diffusion of these ions from the bulk of the solution, and the observed catalytic wave shows some features of diffusion current. Some effects observed in cysteine solutions containing low concentrations of Ni^{2+} can be explained in this way[132]. The Ni^{2+} bound in catalytically active complexes is discharged relatively slowly, and the complex is therefore able to take part in the catalytic process several times before the Ni^{2+} is discharged. Hence, the catalytic current is several times larger than the diffusion current of Ni^{2+} ions[132]. The discharge of metal from the complex has recently been demonstrated[136] with the help of radioactive cobalt ions.

The increase in the catalytic activity of thiols resulting from complex formation with Co^{2+} is probably due to the gain of two charges by the catalyst, which must considerably assist electron transfer to such species.

Co^{2+} and Ni^{2+} ions increase the catalytic activity of pyridine[133] as well as that of sulphur compounds.

Organic compounds containing sulphur show a high surface activity at the mercury–solution interface. Their catalytic waves are definitely of the "surface" types, and are described by the equations for surface waves[81]. Sunahara[122] examined the waves produced by cystine and by some of its derivatives with blocked amino- (*NN*-diacetylcystine) or carboxy- (cystine diethyl ester) groups, and showed that blocking of the amino-groups leads to total loss of catalytic activity, whereas esterification has practically no effect on the catalytic wave. Thus, we may assume that the catalytic action of catalysts containing both amino- and mercapto-groups is mainly associated with the amino--groups, whereas the SH groups are primarily responsible for the adsorbability of the catalyst. This hypothesis accounts for Ivanov's observation[130] of a parallelism between the effectiveness of a catalyst as a maximum suppressor (*i.e.* its adsorbability) and the height of the catalytic wave at equal analytical concentrations. The adsorbability of catalysts, which determines the limiting catalytic current under otherwise identical conditions, increases with the size of the molecule and with the number of SH groups, whereas the number of amino-groups per unit weight of catalysts of similar structure is almost independent of the size of the catalyst molecule. This explains the rough proportionality, reported by Ito[131], between the increase in catalytic activity and the increase in the number of cysteine residues in the molecule of protein catalysts.

It is interesting to note that the normal falling off of catalytic waves in albumin solutions can be avoided by greatly increasing the concentration of albumin at constant concentration of buffer solution and cobalt ions (see, for example, Figs. 3 and 4 on pp. 115 and 117 of Brdička's article[3], and Basinski *et al.*[132]). It follows that under these conditions the rate of formation of the catalytically active complex is no longer determined by the concentration of the protein, and that protein desorption at more cathodic potentials does not cause a decrease in catalytic current.

2. The Splitting of Albumin Waves

Catalytic waves in albumin solutions containing cobalt ions, unlike the waves produced by many amino-acids, often have a characteristic "double hump" shape. A study[93] of this splitting of catalytic waves led to the suggestion that two catalysts, of different catalytic and adsorption properties, must be present in solution.

Numerous observations indicate that the catalyst responsible for the first albumin wave is the less adsorbable. Thus, addition of a surface-active substance such as gelatine decreases the height of the first step, but leaves the second step almost unchanged (see, for example, Fig. 4 of Marha's paper[134]). The smaller temperature coefficient of the first wave[135] also points to the same conclusion (on the assumption that the chemical reactions which determine the height of the two waves have similar activation energies).

Addition of ethylenediaminetetraacetic acid (EDTA) to Brdička's solution initially decreases the second wave (see Fig. 4 of Ref. 129). This is obviously due to the sequestering effect of EDTA, which lowers the concentration of Co^{2+} ions in solution, but it involves the further assumption that the Co^{2+} ions are more firmly bound to the protein in the catalyst responsible for the first wave than in the second catalyst.

If the solution contains a complexing agent with which cobalt can form a more stable complex than it can with the second catalyst (but less stable than with the first), the polarograms should retain only the first albumin wave. Ito[131] has observed this phenomenon by working with a solution of tris(ethylenediamine)cobalt.

Various chemical effects which influence the height of albumin waves, such as the effects of higher fatty acids[134] or of formaldehyde[137], can be explained in terms of blocking of catalytically active centres or of interaction with groups involved in complex formation, or alternatively by postulating a change in the adsorbability of the catalyst.

VI. CATALYTIC HYDROGEN WAVES AND THE STRUCTURE OF ORGANIC CATALYSTS

1. General Remarks

Knobloch[14] was the first to point out that the decrease in hydrogen overvoltage at a dropping mercury electrode caused by a series of heterocyclic catalysts increases in proportion to the acidity of the catalyst. Data for different classes of organic catalysts, obtained by von Stackelberg *et al.*[18], show that catalytic hydrogen evolution often increases with decreasing pK_A in a series of structurally similar catalysts. A qualitative explanation readily follows from the proposed mechanism for the catalytic wave. According to Shikata and Tachi's rule[138], discharge of the electrochemically active acidic form of the catalyst is facilitated by increasing the electronegativity of the residue attached to the group undergoing reduction[50]. But it is well known that the introduction of an electronegative group into an acid molecule also lowers pK_A.

The height of the catalytic wave, on the other hand, is usually greater when pK_A of the catalyst is large[14,139]. This is because, other conditions being the same, the protolytic equilibrium between the two forms of the catalyst (process I) is displaced towards the electrochemically active (acidic) form when pK_A of the catalyst increases.

2. Reversible Bulk Catalytic Waves in Buffered Solutions

The quantitative relationship between catalyst structure and the nature of the catalytic wave is most conveniently investigated by discussing bulk, reversible catalytic waves, in the absence of complicating adsorption phenomena. To this end, a study of the bulk catalytic waves produced by pyridine, the picolines, and 2,6-lutidine has been made[65].

Fig. 3 shows the variation of $(i_{lim}/i_d)^2$ with concentration of undissociated boric acid at a constant pH of 8.40. It can be seen that the slope of the linear plots, which is a measure of the rate of protonation, depends on the nature of the catalyst. Values of ρ were calculated from Eqn. (14) (for the method of evaluating k_d, needed in the calculation of ρ, see later), and were used to derive the individual rate constants shown in Table 1. In a series of structurally similar catalysts the protonation rate constant for a particular acid (k_A) should increase with pK_A of the catalyst, as required by Brønsted's relation.

When H_3BO_3 and veronal are used as protonating agents, $k_{H_3BO_3}$ and $k_{veronal}$ for the 2-methyl derivatives (see Table 1) are much lower than the Brønsted value owing to steric hindrance[140]. Thus, steric factors can have a profound influence on the height of catalytic waves.

When the buffer capacity of the solution is increased at constant pH, the $E_{1/2}$ value for the bulk catalytic waves of these compounds becomes more negative, the slope $\Delta E_{1/2}/\Delta \log\rho$ being approximately -20 mV as required by Eqn. (17). The half-wave potential becomes more negative also with increase in pH (see Fig. 4).

The standard redox potential E_0 for reaction (II) can be evaluated by means of Eqn. (17). By substituting the values[26,66] of k_d for pyridine and for 2,6-lutidine into Eqn. (17), E_0 values of -1.626 V and -1.715 V (w.r.t. the saturated calomel electrode) were obtained for the discharge of their ions. E_0 is related to pK_A by the expression

$$E_0 = \text{const} - \frac{2.3RT}{F} pK_A . \qquad (37)$$

The experimental data for pyridine and 2,6-lutidine give -1.302 V and -1.312 V respectively for the constant in Eqn. (37). In view of the limited accuracy of the measurements[26,66] of k_d, we may conclude that these values do not differ significantly, and that the k_d values themselves are correct to within a power of ten. Putting const = -1.307 V, the values of k_d for the picolines (Table 1) were obtained from Eqns. (17) and (37), and used to calculate ρ by means of Eqn. (14). The relationship between $E_{1/2}$ for the catalytic wave and pK_A for the catalyst is evident from Eqns. (17) and (37).

3. Bulk Waves in Unbuffered Media

The rate constants for the protolytic interaction of the pyridine homologues with water were determined[63] from the effect of catalyst concentration on the limiting currents of catalytic polarographic waves in unbuffered solutions (see Fig. 8). The rate constants for protonation by water (k_1) and deprotonation by OH^- (k_2) of the same series of compounds in 0.5 M KCl at 25° are listed in Table 2.

The k_1 values increase with pK_A of the catalyst, as required by the Brønsted equation for the protonation of bases of a given structure by a given acid:

$$\log k_1 = \log G + \beta pK_A . \qquad (38)$$

With the exception of 2-picoline, the k_1 values of the catalysts follow Brønsted's Eqn. (38) to an accuracy[63] of ±5%.

TABLE 1. Properties of pyridine and its methyl derivatives.

	Pyridine	2-Picoline	3-Picoline	4-Picoline	2,6-Lutidine
pK_A (25°C, 0.5 M KCl)	5.50	6.15	5.90	6.19	6.83
k_d, litre mole^{-1} s^{-1}	$5.0\cdot10^9$	$3.8\ 10^7$	$1.4\cdot10^8$	~$3\cdot10^5$	$1.5\cdot10^6$
E_0, V (sat. cal. el.)	−1.632	−1.670	−1.655	−1.673	−1.710
$k_{H_3BO_3}$, litre mole^{-1} × × s^{-1}	$7\ 10^3$	$1.5-2\cdot10^3$	$7-10\cdot10^3$	$1-2\cdot10^4$	~100
$k_{veronal}$, litre mole^{-1} × × s^{-1}	$1.3\ 10^5$	$4\ 10^4$	$1-2\cdot10^5$	$3-6\cdot10^5$	~$8\cdot10^3$
N-Methiodides in 0.5 M KCl					
$E_{1/2}$, (~0.5×10^{-3} M)	−1.522	−1.60	−1.560	−1.671	−1.698
$10^5 D$, cm^2 s^{-1}	1.05	1.05	0.95	1.00	1.10

TABLE 2. Some constants of pyridine, the picolines, and 2,6-lutidine in 0.5 M KCl at 25°.

Compound	pK_A	k_1, litre × × mole^{-1} s^{-1}	$10^{10}k_2$, litre × × mole^{-1} s^{-1}	ϵ_0'', V ($c=24\times10^{-6}$ M, saturated calomel electrode)	E_0, V (saturated calomel electrode)
Pyridine	5.50	5.5	9.8	−1.733	−1.614
2-Picoline	6.15	10.1	4.0	−1.800	−1.675
3-Picoline	5.90	8.0	5.5	−1.775	−1.656
4-Picoline	6.19	12.5	4.5	−1.869	−1.699
2,6-Lutidine	6.83	2.6	2.1	−1.875	−1.732

With 2-picoline the error is 12%. The coefficients of Brønsted's equation for this particular reaction are: $\log G = -2.15$; $\beta = 0.5$.

Brown and his coworkers[140,141] showed that the rate constants for chemical reactions involving the nitrogen atom of pyridine derivatives with a CH_3 group in position 2 are significantly lower, as a result of steric hindrance, than the values predicted by the linear rule for free energy changes (see, for example, Pal'm[142]). For any given 2-substituted pyridine derivative, the steric effect increases with the size of the species attacking the nitrogen atom of the pyridine ring[141].

Steric effects are also apparent, as mentioned earlier, in the protonation of pyridine homologues by boric acid and by veronal. However, no steric hindrance is observed when the 2-methyl derivatives of pyridine are protonated by water: this may be due to the small size of the water molecule. Protonation of these compounds by hydronium ions is also free from steric hindrance effects[141].

An increase in the pK_A of the catalyst shifts the wave towards more negative potentials in unbuffered as well as in buffered solutions (see Fig. 9). The characteristic potentials ϵ_0'', listed in Table 2, are convenient for comparison purposes. Inspection of Eqn. (25) shows that ϵ_0'' depends primarily on the E_0 value of the redox system, which decreases linearly [see Eqn. (37)] with the pK_A of the species undergoing discharge.

E_0 can be determined by means of Eqn. (25) from experimental values of ϵ_0'' and of the rate constant. The E_0 values listed in Table 2, obtained in this way, are obviously less accurate than the values measured in buffered solutions (see Table 1).

4. Irreversible Surface Waves

The relationship between irreversible surface catalytic hydrogen waves and the structure of the catalyst is complicated by adsorption phenomena which increase the catalytic current, but can also displace the wave towards less cathodic potentials.

In a series of catalysts of comparable adsorbability, the half-wave potential $E_{1/2}$ (or the "half-maximum" potential, which is much easier to determine) varies with the pK_A of the catalyst according to one of the modified forms of Hammett's equation (see, for example, Pal'm[142] or Zuman[143]): the wave moves in the negative direction as pK_A increases. The limiting current, as already pointed out, increases with the pK_A of the catalyst. Numerous examples of this type of behaviour are to be found in some of the papers already mentioned[14,18,139].

Zuman and Kuik[144] have shown that the catalytic activity of pyrimidine in Co^{2+} solutions is increased by substituents in the 5-position in the following sequence: $OH < NH_2 < SH$. They attribute the higher activity to changes in acid properties and in the ability to form complexes with Co^{2+}.

Lamprecht *et al.*[21] established that the nature of the catalytic wave depends on the type of complex formed by the sulphur-containing catalyst and Co^{2+}. Thus, if complex formation involves, besides SH and SS groups, some neighbouring carboxy-groups, the catalytic wave occurs immediately beyond the discharge potential of cobalt, and shows the characteristic falling off observed in solutions of cysteine and Co^{2+}. If Co^{2+} in the complex is coordinated to sulphur and also to an NH_2 or NH group in the same molecule, the resulting wave is somewhat lower, and, instead of falling off, shows something in the nature of a limiting current plateau. If the molecule contains no ligand groups other than SH or SS, polarograms taken in ammoniacal cobalt solutions show only the rising section of the wave before the discharge potential of the base electrolyte, but no limiting current.

Stevančevič published some interesting observations[145] on the catalytic activity of quinoxaline-2,3-dithiol in Co^{2+} and Ni^{2+} salt solutions. The catalytic wave in nickel solutions is significantly lower than in cobalt solutions, and occurs at less negative potentials. Assuming approximately equal adsorbabilities for the complexes formed by quinoxalinedithiol with nickel and with cobalt ions, the observed difference between the catalytic waves must be attributed to a higher pK_A for the Co^{2+} than for the Ni^{2+} complex.

Toropova and Elizarova[146] showed that complex formation between sulphur compounds and Fe^{2+} (as well as Co^{2+} and Ni^{2+}) can give rise to catalytic activity. When metal ions which can attach themselves to a thiol more firmly than can Ni^{2+} are added to the polarographic solution, the height of the catalytic hydrogen wave decreases[146-148].

The dependence of the catalytic wave on the pK_A of the catalyst has been used[149] to evaluate, approximately, unknown pK_A values of catalytically active compounds.

When the catalysts differ in their surface activity, the height of the catalytic wave increases with the adsorbability of the compound[130,131]. Surface waves are extremely sensitive to slight changes in the structure of the catalyst: Zuman[150] reports that the second polarographic wave of *erythro*-phenylcysteine in ammoniacal $CoCl_2$ solution is almost twice as high as the corresponding wave of the *threo*-isomer.

5. Catalytically Active Organic Compounds

The catalytic activity of organic catalysts is determined by the ability of the catalyst to add on a proton and form an 'onium' compound. Thus, catalytic waves are observed in solutions of amines (but not tetrasubstituted amines!), thiols and sulphides, phosphines[92], and arsines[151-154]. Knobloch[15,155] has recently made a detailed study of the catalytic hydrogen waves produced by oxonium compounds (derivatives of chromone). Ryvolová[156] also observed catalytic hydrogen evolution in the presence of catalysts of the oxonium type (the products of electrochemical reduction of unsaturated diketones containing methoxycarbonyl groups). Zhdanov and Polievktov[157] described catalytic waves due to diphenylcyclopropenone in acid solutions.

VII. ALTERNATIVE THEORIES OF CATALYTIC HYDROGEN WAVES

A number of theories and schemes, differing from that presented here, have been put forward to account for the nature and mechanism of catalytic hydrogen waves. We shall consider them briefly in the present section.

One of the earliest theories was formulated by Brdička to explain the mechanism of catalytic waves in solutions of sulphur compounds. This worker visualised hydrogen being split off, at the electrode, from the SH group of the thiol, followed by protonation of the RS^- anion by acidic constituents of the solution. A short account of this theory has already been presented in Section V. Brdička's views are widely known, and are described in most polarographic textbooks: we shall not consider them further, except for pointing out that Brdička's theory is not applicable to catalytic waves due to nitrogenous organic bases.

Kirkpatrick[11], in his study of catalytic hydrogen evolution in the presence of many different alkaloids, proposed that the catalytic act consists in the capture of an electron from the electrode by the alkaloid, followed by transfer of the electron to a hydrogen ion in solution. According to Kirkpatrick, the catalytic activity of an alkaloid is determined by its "electron capacity", *i.e.* by its ability to extract electrons from the cathode.

Knobloch[14] applied Brdička's mechanism to the catalytic waves produced by heterocyclic and aromatic amines. Like Brdička, he assumed that the catalyst accelerates the formation of molecules from the atomic hydrogen evolved at the cathode and thus lowers the hydrogen overvoltage (in accordance with Heyrovský's theory[158] of hydrogen overvoltage). In his more recent paper[15], however, Knobloch adopts the mechanism for the formation of catalytic waves put forward by von Stackelberg and his coworkers[17-19].

Von Stackelberg's mechanism comes nearest to that proposed by the present author. According to von Stackelberg[17-19], the catalyst is active only when adsorbed on the electrode. By accepting a proton, it is converted into the electrochemically active cationic form, which is irreversibly discharged at the electrode, evolving hydrogen and regenerating the catalyst in its basic form. Von Stackelberg and his coworkers do not consider the mechanism of the last stage of the process, following the electrochemical act. Hence, with the exception of the last stage, von Stackelberg's mechanism is indistinguishable from the particular case of irreversible surface waves in the author's mechanism. Von Stackelberg's mechanism does not account for all the facts: as we saw in the previous Sections, there are catalytic processes other than irreversible surface waves. Protonation can occur in the layer of solution adjacent to the electrode, *i.e.* without involving adsorption of the catalyst, which is a prerequisite in von Stackelberg's theory, and electron transfer to a protonated catalyst species can occur fast enough to make the electrochemical stage reversible.

The view (held by von Stackelberg and his coworkers) that the catalyst can only be protonated by hydronium ions is probably erroneous. Other acids present in solution are thought to contribute to the process only after dissociation, with formation of hydronium ions:

$$HA \rightarrow H^+ + A^-, \qquad (V)$$

$$B + H^+ \rightarrow BH^+. \qquad (VI)$$

On the basis of these concepts, von Stackelberg and his coworkers[159-161] even tried to determine the rate constants for the dissociation of acids HA from the catalytic currents observed in solutions of these acids (and also, by applying the method of Rüetschi[162], from kinetic currents limited by the rate of protonation). However, the processes investigated by these workers were in fact limited mainly by the rate of the direct interaction of HA with B (see, for example, Refs. 33, 34, 82, 163–165).

Thus, the dissociation of water into its ions

$$2H_2O \rightarrow H_3O^+ + OH^- \quad (k = 2 \times 10^{-4}\ s^{-1}\ ^{166})$$

(an essential condition in von Stackelberg's theory) cannot possibly account for the catalytic currents observed in unbuffered solutions, which corresponds, as already pointed out, to the rate of protonation of the catalyst by water itself (for pyridine, $k_1 = 5.5$ litre mole^{-1} sec^{-1}).

If protonation of a catalyst by an undissociated acid of the type HA involved a preliminary dissociation stage, no steric hindrance would be observed in the protonation of 2-picoline and 2,6-lutidine by undissociated boric acid and veronal[63], since there is no hindrance when these compounds are protonated by water or by hydronium ions[141].

To conclude this brief survey of theories of the catalytic hydrogen wave, we shall discuss Frumkin's shrewd explanation[28,167] of the ease with which the cations of the catalyst are discharged (as compared with the discharge of hydrogen ions). Frumkin confines himself to discussing a situation in which the purely electrochemical reaction is the slowest step of the catalytic process, and the catalyst exists mainly as the electrochemically active action BH^+ both in solution and in the adsorbed state (*i.e.* $\sigma \ll 1$). Assuming that the discharge of BH^+ and H_3O^+ involves identical transfer coefficients α, Frumkin applies Brønsted's equation (relating the rate constant of an electrode process to the dissociation constant of the acid undergoing discharge) to the problem of calculating the rate constants for electron transfer to BH^+ and H_3O^+. It can be shown that BH^+ will be discharged faster than H_3O^+ in the same solution only if BH^+ is a cation and its specific adsorption is considerable. Then, and only then, does the effect of the electrical double layer structure favour the discharge of BH^+ significantly much more than the discharge of H_3O^+. The theory assumes, however, that the product of the electrochemical reaction is an adsorbed hydrogen atom, rather than a BH radical. Thus it cannot explain, among other things, the formation of reversible catalytic waves. The theory is likewise inapplicable to the case of $\sigma \gg 1$, *i.e.* to catalysts which exist mainly in their basic (unprotonated) form.

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NEW ASPECTS OF THE CHEMISTRY OF COMPLEXES OF SELENIUM AND TELLURIUM

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I. INTRODUCTION

The growing interest in the chemistry of rare and dispersed elements, which include selenium and tellurium, is connected with the development of new branches of technology — automation, telemechanics, and semiconductor technology.

In the Periodic System selenium and tellurium lie between sulphur, a typical non-metal, and polonium, a metal. This position determines the most important physical and chemical properties of these elements. As regards electrical conductivity, tellurium recalls a metal while selenium is a semiconductor. Selenium and tellurium and their compounds are widely used in semiconductor technology for the production of thermoelements, systems for stabilising temperature, and in radio technology.

Because of its high resistivity and its ability to pass current only in one direction, selenium is used as a rectifier. Its electrical conductivity increases 1000 times on exposure to light and on this is based its use in the production of photometers and photoelectric cells. Selenium is also used as a luminophore in the manufacture of screens permitting a high resolution, in radar systems, television receivers, and other apparatus. In metallurgy, addition of selenium and tellurium to cast iron, steels, and other alloys improves the structure and workability of these materials, and raises the hardness and strength of the alloys. Selenium is also used in the rubber industry as a catalyst for organic synthesis, and in the glass industry.

In spite of the considerable scale of world production of selenium (845 tonnes in 1959, excluding the USSR) the demand for it in semiconductor technology is still not satisfied. The consumption of selenium in other branches of industry is gradually decreasing [*sic* (Ed. of Translation)] and the need for new sources for the production of selenium and tellurium arises more clearly; the possibility of finding substitutes for selenium is also being studied.

In the USSR, the problem of a complete and rational separation of these elements on an enormous scale, from sulphide ores containing selenium and tellurium, is very substantial.

The wide use of selenium and tellurium in semiconductor technology creates new problems as regards their preparative and analytical chemistry. For semiconductors these elements and their compounds are required in a super-pure state. In analytical chemistry problems arise in the development of rapid and accurate methods for determining selenium and tellurium in various materials — mineral raw material, semiconductors, steels, alloys, etc.

Methods of obtaining pure selenium, tellurium, and their compounds have been discussed by Novoselova, Pashinkin, and Popovkin[1].

A number of new analytical methods for determining selenium and tellurium have been described in recent years.

The reaction of selenium with 3,3′-diaminobenzidine was first mentioned[2] in 1948, but a number of papers on the use of this highly sensitive and specific reaction for the determination of selenium in various types of material have appeared in the last two or three years. A new, very sensitive reagent for the determination of tellurium — Bismuthol-II — was proposed in 1960–1961.[3,4] A series of papers on the reaction of tellurium with thiourea appeared in 1957–1962. There is a very large amount of published work on tellurium complexes. Apart from the long-known acido-complexes with hydrogen halides (M_2TeX_6 type), complexes of tellurium with nitrogen- and sulphur-containing ligands have been examined.

A study of the compounds of selenium and tellurium shows that these elements often differ sharply in their properties: tellurium forms a large group of complexes, whereas only isolated examples of selenium complexes are known. The difference in the ability of these elements to form complexes opens up great possibilities of analytical chemistry in the development of sensitive and specific methods for their determination.

An attempt is made in this review to generalise from the diverse, and often contradictory, publications, mainly in recent years, on complexes of selenium and tellurium and their application to preparative and analytical chemistry. The properties of the simple compounds are not discussed; regarding them see, for example, Kudryavtsev[18] and Brasted[19].

1. Hydrogen Halogeno-Acids of Selenium and Tellurium and Their Salts

For tellurium, hydrogen halogeno-acids of composition $TeCl_4.HCl.5H_2O$, $TeBr_4.HBr.5H_2O$, and $TeI_4.HI.8H_2O$, obtained by the action of the corresponding acids on $TeCl_4$, are known[20,21]. They are formed as needle-shaped prisms, the chloride being yellow, the bromide red, and the iodide black. They are very hygroscopic and easily deliquesce in the air, and on heating they easily lose a molecule of HX.

The oxide fluorides $TeF_4.3TeO_2.6H_2O$, $TeF_4.TeO_2.2H_2O$, and $TeF_4.TeO_2.H_2O$, for which the existence of the complex anion $[TeO_2F_2]^{2-}$ is proposed, have also been described[20,22].

When CsF was added to a solution of TeF_4 in HF the compound $CsTeF_5$ was obtained[23]. Other pentafluorotellurates(IV), $NH_4TeF_5.H_2O$, $KTeF_5$, and $Ba(TeF_5)_2.2H_2O$, are also known.

A compound with oxine, $HTeI_5.2Oxin.10H_2O$, was isolated from a solution in HI containing tellurium[24].

Aynsley[25] obtained a fluoro-complex of tellurium and pyridine $[C_5H_5NH]TeF_5$ and a series of halogeno-complexes with urea $[CON_2H_5]TeX_5$, where X = Cl, Br, I.[26]

In the compounds with urea the stability of the $[TeX_5]^-$ anion increases from the chloro- to the iodo-complex, since the chloro-complexes are easily converted into the bromo- and iodo-complexes under the action of the corresponding HX. Several authors were unable to obtain fluoro--complexes with urea.

Numerous hexahalogenotellurates(IV) are known — with the chlorides, bromides, and iodides of K, Rb, and Cs,[27,28] and also the chlorides and bromides of ammonium and thallium[29–31].

However, it has so far not been shown definitely that the free hexahalogeno-acids of Te^{IV} can be obtained. Some authors[32] state that $H_2TeCl_6.2H_2O$ can be obtained as well--formed yellow crystals by dissolving freshly precipitated TeO_2 in HCl (1 : 1), and that these give H_2TeBr_6 on reaction with HBr.

Dobrowolski[29,30] and Yakovleva and Troitskii[33] attempted to reproduce Ripan's experiments[32]. However, the hexahalogeno-acids of tellurium could not be obtained by him. Dobrowolski[29,30] obtained the ammonium and thallium salts $(NH_4)_2TeCl_6$ and Tl_2TeBr_6.

The stability of compounds containing $[TeX_6]^{2-}$ ions apparently depends to a considerable extent on the degree of polarisation caused by the cation. The strongly polarising hydrogen ion therefore makes the $[TeX_6]^{2-}$ anion unstable, and this may explain the instability of acid solutions containing the coloured $[TeI_6]^{2-}$ ion[34–36]. It is therefore possible to agree with Dobrowolski[29,30] who doubts the possibility of isolating H_2TeCl_6 and H_2TeBr_6 in the pure state. It is clear that for the same reason the hexahalogenotellurates(IV) of lithium and sodium were not obtained, as these are cations which also possess a high polarising power. On the other hand, large weakly polarising cations — K^+, NH_4^+, Tl^+, Rb^+, Cs^+ — form quite stable hexa-chloro-, -bromo-, and -iodo-tellurates(IV).[27–31]

H_2SeBr_6 was isolated in the pure state from hydrogen halogeno-acids of selenium[37,38]. This acid dissolves in

water without decomposition but decomposes in air with liberation of bromine and colloidal selenium. The analogous hydrogen hexachloroselenate(IV) has not been obtained. The compounds $SeO_2.2HCl$ and $SeO_2.2HBr$ were shown to be identical with the hydrates $SeOCl_2.H_2O$ and $SeOBr_2.H_2O$.[39]

Potassium and ammonium hexachloroselenates(IV) were obtained as yellow crystalline materials which decompose easily in the air[40]. $(NH_4)_2SeBr_6$, K_2SeBr_6, and Rb_2SeBr_6 are also known[27,41].

Examination of solutions containing compounds of selenium and chlorine or bromine[42,43] indicates the existence of some types of complex in solution and that, under certain conditions, hydroxyhalides of selenium with an Se : Cl(Br) ratio of 1 : 2 may be formed.

Spectrophotometric examination of hydrochloric acid solutions containing Te^{IV} showed[44] that more than one type of ion exists in such a solution. At high HCl concentrations (9–12 *N*) two maxima, at 269 and 376 mμm, are observed in the absorption spectrum. In 6 *N* HCl the maximum at 269 mμm disappears and that at 376 mμm is noticeably reduced. Since halogeno-complexes of tellurium are coloured, solutions containing these compounds are used in the presence of hydrochloric acid, bromides, and iodides in photometric methods of determining tellurium[24,34-36,45-47].

The difference in the properties of compounds of selenium and tellurium present in hydrochloric acid solution and the possibility of the formation of several types of complex ion by these elements are used in extraction and ion-exchange methods of separating selenium and tellurium.

A study of the sorption of selenium and tellurium by ion exchangers in hydrochloric acid solution allowed Ermakov and coworkers[48] to perfect conditions for the quantitative separation of tellurium and selenium on EDE-10 anion--exchange resin†.

Tribenzylamine in chloroform was used as extractant in the separation of selenium and tellurium[49]. Using this solvent it was found possible to separate selenium and tellurium completely from 4–6 *N* HCl. Tellurium passes completely into the organic phase, while selenium remains in the aqueous solution. *N*-Dodecyltrialkylmethylamine in xylene has also been used as solvent.

The use of tributyl phosphate for the separation of selenium and tellurium, of telurium(IV) and tellurium(VI), and the removal of selenium and tellurium from iodine and sulphate ion has been described by Inarida[50-53]. It was established that tellurium(IV) is quantitatively extracted from 4–12 *N* HCl by 30% tributyl phosphate in kerosene, and a higher concentration of hydrochloric acid, about 6–12 *N* HCl, is required for selenium to pass into the organic phase. Thus the acidity must be made 4–5 *N* in HCl for the separation of selenium and tellurium. The use of 20% tributyl phosphate in kerosene as solvent allows Te^{VI} and Te^{IV} to be separated in hydrochloric acid solution (4–10 *N*). If 100% tributyl phosphate is used, the separation takes place over a still greater range of hydrochloric acid concentration, from 2 to 10 *N*.

† EDE-10P is a polyfunctional weakly or strongly basic anion--exchange resin prepared by the condensation of polyethylene-polyamines with epichlorohydrin, and contains secondary, tertiary, and quaternary nitrogen groups (Ed. of Translation).

Extraction with 100% tributyl phosphate from 0.2 *N* HCl is used to remove iodide ion[53]. Under these conditions the iodide passes quantitatively into the organic solvent phase. The acidity is then increased and tellurium(IV) is extracted from 4 *N* HCl.

Sulphate ion is removed in 4–12 *N* HCl with 30% tributyl phosphate in kerosene.

Selenium and tellurium are removed from other elements using isobutyl methyl ketone, 99% of the selenium and 96% of the tellurium being extracted from hydrochloric acid solution[54].

The use of a hydrochloric acid medium for the separation of selenium and tellurium by extraction is based on the difference in stability of their halogeno-complexes. An examination of separation methods described in the literature shows that Te^{IV} forms stable halogeno-complexes over a wider range of acidity than Se^{IV}, and the latter over a wider range than Te^{VI}. Extraction of selenium and tellurium with amines and tributyl phosphate under these conditions is probably connected with the formation of definite chemical compounds of the type solvent–acido-complex of Se or Te.

II. COMPLEXES OF SELENIUM AND TELLURIUM WITH LIGANDS CONTAINING NITROGEN

1. Compounds of Selenium and Tellurium with Organic Bases and Ammonia

The reaction of tellurium tetrachloride or tetrabromide dissolved in anhydrous ether, glacial acetic acid, benzene, alcohol, or acetone with aromatic amines gives the following compounds[55-60]:

$(C_6H_5NH_2)_2.TeBr_4$, $[(C_6H_5)_2NH]_2.TeBr_4$,
$(BrC_6H_4NH_2)_2.TeBr_4$, $(C_{10}H_7NH_2)_2.TeBr_4$,
$[C_6H_4(NH_2)_2].TeBr_4$, $[C_7H_6(NH_2)_2].TeBr_4$,
$[NH_2C_6H_4.C_6H_4NH_2].TeBr_4$, etc.

All these compounds crystallise well, are stable in air, but are decomposed by water; they are insoluble in ether, ethanol, chloroform, benzene, and carbon tetrachloride, but dissolve easily in acids. Some derivatives, for example the compounds with toluidine and *o*-phenylenediamine, are easily soluble in acetone. Tronev and coworkers[57] obtained the following compounds of $TeCl_4$ and $SeCl_4$ with ethylenediamine (En), pyridine (Py), aniline (An), thiourea (Thio), and ammonia:

$SeCl_4.4NH_3$, $SeCl_4.2Thio$, $SeCl_4.2En$,
$TeCl_4.2NH_3$, $TeCl_4.6NH_3$, $TeCl_4.2En$,
$.TeCl_4.2En.2NH_3$, $TeCl_4.2An$, $TeCl_4.2An.2NH_3$,
$TeCl_4.2Py$, $TeCl_4.2Thio$, $TeCl_4.6Thio$.

The thermal stability of these compounds was studied and it was shown that the bond between selenium or tellurium and the ligand containing nitrogen is characterised by a fairly high stability, especially in the case of ethylenediamine.

$TeBr_4$ forms compounds of the composition $(C_4H_4N_2).TeBr_4$ with diazines (pyrimidine, pyrazine, etc.). Similar 1 : 1 complexes were obtained with N_4S_4, $N_4S_4H_4$, and dioxan[26].

When heated in HBr solution the compounds with diazines $(C_4H_4N_2).TeBr_4$ are converted easily into crystalline salts $(C_4H_5N_2).TeBr_5$. The corresponding chlorides and iodides

can be obtained analogously. Aynsley [26] showed that for the diazine derivatives the stability of the TeX_5^- anion increases from the chloride to the iodide.

In the case of fluorides a white crystalline compound with pyridine $(C_5H_5N).TeF_4$ was obtained but $(C_5H_5N)_2.TeF_4$, which is expected by analogy with the chlorides and bromides, where the number of amine molecules combined with one $TeCl_4$ molecule is determined by the number of amino-groups in the molecule, was not obtained.

Tetrafluoropyridinetellurium(IV) $(C_5H_5N).TeF_4$ undergoes no change in air but is easily decomposed by water to form tellurous acid. In HF solution yellow crystalline pyridinium pentafluorotellurate(IV) $(C_5H_5NH)TeF_5$ is formed. This compound could not be converted into the corresponding chloro-, bromo-, or iodo-compound by using the appropriate hydrogen halide because in all cases the compounds $(C_5H_5NH)_2TeX_6$ were formed.

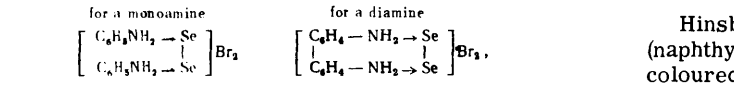
With urea, pentahalogenotellurates(IV) with the general formula $(CON_2H_5).TeX_5$, where X = Cl, Br, or I, were obtained [26].

Dipyridinium hexafluorotellurate(IV) $(C_5H_5NH)_2TeF_6$ is obtained in a solution of TeO_2 and pyridine in concentrated HF. When treated with HI it gave dipyridinium hexaiodotellurate(IV) $(C_5H_5NH)_2TeI_6$, and it is easily converted by the action of HCl and HBr, into $(C_5H_5NH)_2TeCl_6$ or $(C_5H_5NH)_2TeBr_6$. Dipyridinium hexaiodotellurate(IV) is formed on treating any other hexahalogenotellurate(IV) with hydriodic acid.

Many hexahalogenotellurates(IV) of amines (primary, secondary, and tertiary) [61-64], *N*-acetylamine [65], and alkaloids [66] are at present known and their properties have been studied. In some acetyl derivatives of hexahalogenotellurates(IV) three or four *N*-acetylamine molecules are combined with one H_2TeCl_6 molecule [65].

Whereas with tellurium the complexes with amines (and with some other organic bases) are numerous, for selenium only isolated examples are known. Tronev [57] obtained the compounds $SeCl_4.4NH_3$, $SeCl_4.2Thio$, and $SeCl_4.2En$. Compounds of amines with selenium oxide halides are also known: $2SeOCl_2.3(CH_3)_2NH.HCl$, $SeO_2.(CH_3)_2NH.HCl$, $2SeBr_4.SeBr.3(CH_3)_2NH.HBr$, $SeBr_4.2(CH_3)_2NH.HBr$, and some others [67].

The amino-derivatives of selenium monobromide [58,59]:



have been obtained with aniline, *o*-toluidine, *m*-toluidine, *o*-anisidine, benzylamine, α-naphthylamine, benzidine, and some other amines. These compounds are stable in air, insoluble in water and organic solvents, are hydrolysed by water on boiling, and are decomposed by dilute acids and alkalis.

There is little published information on the composition, structure, and properties of the ammines of selenium and tellurium. It is known from old work [31,68-70] that ammines, amides, imides, and nitrides of various compositions can be formed in the reaction of $SeCl_4$ and $TeCl_4$ with ammonia. SeO_2 reacts with liquid ammonia to give selenium nitride $(NSe)_x$. [71,72]

Tronev and coworkers [57] examined the series of compounds formed by the action of anhydrous ammonia on $TeCl_4$ and $SeCl_4$ at elevated pressure and temperature. $SeCl_4.4NH_3$, $TeCl_4.4NH_3$, and $TeCl_4.6NH_3$, and also compounds of a mixed type $TeCl_4.2En.2NH_3$ and $TeCl_4.2An.2NH_3$ were obtained by this method.

Ammines were converted into amides and ammonium chloride by repeated washing with liquid ammonia.

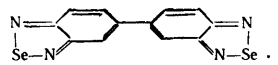
Amino-compounds of selenium, obtained from the reaction of elementary selenium with ammonia and oxygen under pressure at 50–100°, have also been studied.

The reaction of selenium dioxide difluoride with ammonia [74] gives a mixture of the ammonium salts of cyclic triselenimide $(SeO_2NNH_4)_3$ and a homologous series of cyclic polyimidoamides of selenous acid $NH_2SeO_2N(NH_4)_nSeO_2NH_2$. [74]

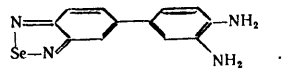
Dostal [75] obtained and investigated the amidoselenates of silver, $Ag(SeO_3NH)$, and of alkali and alkaline earth metals.

2. Compounds of Selenium with 3,3′-Diaminobenzidine and Some Other *o*-Diamines

Selenous acid reacts in hydrochloric acid solution with 3,3′-diaminobenzidine to form a yellow crystalline precipitate which is insoluble in both acidic and alkaline media. Dipiazoselenol, m.p. 292–314°, is formed in solutions containing an excess of selenous acid [2,76,77]

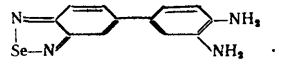


Monopiazoselenol, dark red crystals with m.p. 202°, can be formed when there is insufficient selenium [77].



Tellurium does not react with diaminobenzidine.

A highly sensitive and specific method for determining selenium is based on the ability of the latter to form a yellow coloration with diaminobenzidine in dilute solutions, Monopiazoselenol — 3,4-diaminophenylpiazoselenol — being formed in solution [77]:



Hinsberg [78] first discovered the ability of diamines (naphthylenediamines) to react with selenium and so form coloured solutions.

The method of determining selenium with 3,3′-diaminobenzidine was proposed by Hoste and Gillis [2,76]. Piazoselenol is formed quantitatively in acid medium. As the acidity is increased the intensity of the colour increases but the rate of the reaction falls. The colour of the compound of selenium with 3,3′-diaminobenzidine is stable in 0.1 *N* HCl. The maximum of the absorption spectrum is at 350 mμm and the molar extinction coefficient is 10200.

Further research showed that the sensitivity and specificity of the reaction are increased by extracting the coloured selenium compound with organic solvents — toluene, benzene, chloroform, isopentanol, pentyl acetate, etc. [79]

A pH of 2–3 provides the best conditions for formation of Piazoselenol, the reaction rate being greater in formic acid than in hydrochloric acid. The coloured compound

is extracted with the organic solvents at pH 6–7. There are maxima in the absorption spectrum of the coloured compound in toluene at 340 and 420 mμm, but the reagent absorbs strongly at 340 mμm and therefore the measurement of optical density is usually made at 420 mμm. The molar extinction coefficient at this wavelength is 19 900.

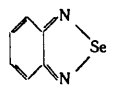
The colour of solutions containing Piazoselenol depends markedly on temperature and is somewhat weakened by the action of light. It is therefore recommended to heat the solutions of Piazoselenol on a water-bath before extraction and to protect the solutions from sunlight after the reaction has been completed[80].

Solutions in toluene which contain Piazoselenol fluoresce in the region of 420 and 580 mμm. The sensitivity of the reaction can be increased considerably by determining the selenium fluorimetrically[77,81,82].

In recent years there have been many published papers on the use of the reaction of selenium with diaminobenzidine — the determination of selenium in sulphur and sulphuric acid[83-88], in tellurium metal[98], in copper, lead, and other metals[90-93], in steels[91,93], and in organic substances and biological materials[91,92,94-97].

Examination of other aromatic *o*-diamines showed that *o*-phenylenediamine is also suitable for the determination of small quantities of selenium[98], the sensitivity of this reaction being somewhat higher than of that with 3,3′-diaminobenzidine[99].

An X-ray structural investigation of the compound of selenium and *o*-phenylenediamine showed that its structure can be represented[100]:



Other diamines also form coloured compounds with selenium, *e.g.* 1,8-naphthylenediamine[101], 4-dimethylamino-1,2-phenylenediamine, and 4-methylthio-1,2-phenylenediamine[91,102].

3. Compounds of Tellurium with Thiourea and Its Derivatives

A compound of tellurium with thiourea was first prepared[103] in 1927, as a yellow crystalline substance with m.p. 165° which is very soluble in alcohol, ether, and other organic solvents.

The reaction of TeX_4, where X = Cl or Br, with thiourea in alcoholic solution gives several compounds[104]: $(SCN_2H_4)_2.TeCl_4$ (m.p. 175°), $(SCN_2H_4)TeBrO_4$ (m.p. 210°), $(SCN_2H_3)_2.TeCl_2$, $(SCN_2H_3)_2TeBr_2$ (m.p. 215°), $(SCN_2H_5)_2.TeCl_6$, $(SCN_2H_5)_2.TeBr_6$ (m.p. 155°), $(SCN_2H_5)_2.TeI_6$, $(SCN_2H_5)_2.TeCl_6.2SCN_2H_5Cl$ (m.p. 155°), and $(SCN_2H_5)_2.TeBr_6.2SCN_2H_5Br$ (m.p. 155°).

Tronev and coworkers[57] obtained several compounds of selenium and tellurium with thiourea: $SeCl_4.2SCN_2H_4$, $TeCl_4.2SCN_2H_4$, and $TeCl_4.6SCN_2H_4$.

Vřeštal[105] isolated a number of thiourea compounds of tellurium from aqueous solutions and showed that all the complexes are derivatives of tellurium(II) because in acid aqueous solution thiourea reduces Te^{IV} to Te^{II}. In solutions of various inorganic acids tellurium(II) forms the following yellow crystalline compounds, which are sparingly soluble in water, with thiourea: $Te(SCN_2H_4)_4Cl_2.2H_2O$ (m.p. 175°), $Te(SCN_2H_4)_2Cl_2$ (m.p. 184°), $Te(SCN_2H_4)_2Br_2$ (two modifications with m.p. 170° and 220°), $Te(SCN_2H_4)_4(ClO_4)_2$ (m.p. 144°), $Te(SCN_2H_4)_4(NO_3)_2.2H_2O$ (m.p. 117°), $Te(SCN_2H_4)_4.SO_4.2H_2O$ (m.p. 141°), and $Te(SCN_2H_4)_4(HC_2O_4)_2.2H_2O$ (m.p. 170°). These compounds are readily soluble in polar solvents but insoluble in non-polar solvents.

In 1959–1961 papers by Foss and coworkers[5-17] described the preparation and some of the properties of complexes of tellurium with thiourea and its derivatives (ethylenethiourea, propylenethiourea, and tetramethylthiourea).

Six-coordinated complexes of tellurium(IV) and tetramethylthiourea (Tmthio) have been obtained: $Te(Tmthio)_2.Cl_4$ (m.p. 153–154°) and $Te(Tmthio)_2Br_4$ (m.p. 176–177°). The dark red crystals of these compounds became dull in the air and they were very rapidly decomposed by water to white H_2TeO_3. When dissolved in an acidic (4 *N* HCl) aqueous methanol solution these substances were rapidly converted into compounds of tellurium(II).

The tetrachloro- and tetrabromo-compounds of tellurium and tetramethylthiourea are the only representatives of compounds of tellurium(IV). All other compounds with thiourea are derivatives of tellurium(II).

The reduction of tellurium(IV) to tellurium(II) by thiourea can be represented by the equation

$$Te^{IV}+4SCN_2H_4+2X^- \rightarrow Te^{II}(SCN_2H_4)_2X_2+[(NH_2)_2CSSC(NH_2)_2]^{2+};$$

the thiourea is oxidised to formalin disulphide.

In an aqueous methanol solution containing Te^{IV} and HCl (or HBr), tetramethylthiourea forms the compounds $Te(Tmthio)Cl_2$ (m.p. 207°) and $Te(Tmthio)Br_2$ (m.p. 226°). The dark red crystals of these compounds are isomorphous and are triclinic.

Four-coordinated complexes with general formula TeR_2X_2, where X = Cl, Br, I, or SCN and R = Thio, Tmthio, Ethio (ethylenethiourea), or Prthio (propylenethiourea), have been obtained.

Thiourea gives $Te(Thio)_2Cl_2$ (m.p. 220°), $Te(Thio)_2Br_2$ (m.p. 220°), $Te(Thio)_2I_2$, and $Te(Thio)_2(SCN)_2$. The crystals of these four complexes are isomorphous and they are *cis*-isomers.

From ethylenethiourea two modifications of the bromide $Te(Ethio)_2Br_2$ were isolated, yellowish brown orthorhombic prisms with m.p. 186° (*cis*-isomer) and reddish yellow monoclinic prisms with m.p. 192° (*trans*-isomer). Both compounds are insoluble in methanol and glacial acetic acid, but readily soluble in dimethylformamide.

$Te(Ethio)_2I_2$, red monoclinic crystals with m.p. 198–200° which are isomorphous with the *trans*-bromide, and $Te(Ethio)_2(SCN)_2$, yellow prisms with m.p. 142–144°, were also obtained.

A chloride, bromide, thiocyanate, and methanethiosulphonate, of which the first two are *cis*-isomers and the last two *trans*-isomers, were prepared from propylenethiourea: $Te(Prthio)_2Cl_2$ (m.p. 199°), $Te(Prthio)_2Br_2$ (m.p. 190°), $Te(Prthio)_2(SCN)_2$ (m.p. 214°), and $Te(Prthio)_2.(S_2O_2CH_3)_2$ (m.p. 172°).

From tetramethylthiourea were obtained the *trans*-isomers $Te(Tmthio)_2Cl_2$ (m.p. 167°) and $Te(Tmthio)_2Br_2$ (m.p. 192°) as reddish orange crystals and two crystalline modifications of *cis*- and *trans*-$Te(Tmthio)_2I_2$.

On forming compounds of the type $Te(Thio)_2X_2$ it is possible to replace the chloride or bromide ions by methanethiosulphonate or benzenethiosulphonate. The following have been isolated: $Te(Thio)_2(S_2O_2CH_3)_2$ (m.p. 130–131°), $Te(Ethio)_2(S_2O_2CH_3)_2$ (two isomers, *cis*- and *trans*- with m.p. 168°), $Te(Ethio)_2(S_2O_2C_6H_5)_2$, $Te(Tmthio)_2(S_2O_2CH_3)_2$, and $Te(Tmthio)_2(S_2O_2C_6H_5)_2$.

No fluoride of the type $Te(Thio)_2X_2$ was obtained.

Foss and coworkers also obtained compounds with three molecules of thiourea (or ethylenethiourea, or propylenethiourea): $Te(Thio)_3(HF_2)_2$, $Te(Ethio)_3(ClO_4)_2$, and $Te(Prthio)_3(ClO_4)_2$. Two modifications of the yellowish green crystals of the last compound, monoclinic and triclinic, were isolated.

Finally, the following complexes with four molecules of thiourea (or its derivatives) were obtained: $Te(Thio)_4Cl_2.2H_2O$, $Te(Thio)_4Cl_2$, $Te(Thio)_4Br_2$, $Te(Thio)_4(SCN)_2$, $Te(Thio)_4(NO_3)_2$, $Te(Thio)_4(ClO_4)_2$, $Te(Thio)_4(HF_2)_2$, $Te(Thio)_4F_2.2H_2O$, $Te(Ethio)_4Cl_2.2H_2O$, $Te(Ethio)_4Br_2.2H_2O$, $Te(Ethio)_4Cl_2$, $Te(Ethio)_4Br_2$, $Te(Ethio)_4(ClO_4)_2$, $[Te(Ethio)_4][TeCl_6]$, $Te(Prthio)_4Cl_2.2H_2O$, and $Te(Prthio)_4.(ClO_4)_2$. Acidic aqueous and ethanol solutions of these compounds saturated with thiourea are stable.

The ethylenethiourea dihydrates are readily soluble in acidic aqueous and methanol solutions, and also in dimethylformamide to form orange solutions which are stable at room temperature. Boiling methanol dissolves about 1.5 g of the substances per 100 ml; anhydrous salts crystallise from such solutions on cooling.

Thiourea, ethylenethiourea, and propylenethiourea form a cationic complex of type $Te(Thio)_4^{2+}$, but not tetramethylthiourea. Steric hindrance probably occurs for the last compound. It was, however, possible to isolate compounds containing two molecules of thiourea and two of tetramethylthiourea: $[Te(Thio)_2(Tmthio)_2]Cl_2$ and $[Te(Thio)_2(Tmthio)_2]Br_2$.

The formation of the coloured $[Te(Thio)_4]^{2+}$ complex in solutions saturated with thiourea is used for the quantitative determination of small amounts of tellurium. Selenium is reduced by thiourea to the element and does not interfere with this determination.

Jilek and Vřeštal[106–110] developed a photometric method for determining tellurium(IV) in the presence of tellurium(VI). They established that the rate of the reaction of Te^{IV} with thiourea depends on the solution pH, concentration of thiourea, and temperature. The maximum coloration is observed in perchloric acid medium (0.8 *N* $HClO_4$) in a solution saturated with respect to thiourea.

Nielsch[111–113] developed a method for determining tellurium by the reaction with thiourea in nitric acid (5–10% HNO_3), phosphoric acid (2–10% H_3PO_4), or sulphuric acid (2–6% H_2SO_4) solutions with a 10–11% thiourea concentration. A maximum was observed in the absorption spectrum at 310–320 mμm. The high sensitivity (1 mg Te in 1 ml) and specificity of the reaction permits the determination of tellurium in copper and selenium, which is especially important for the production of pure selenium.

The determination of tellurium in cast iron by means of the reaction with thiourea is carried out in nitric acid (6% HNO_3).[114]

Leontovitch[115] determined tellurium in ferruginous products using a phosphoric acid medium. Gladyshev[116] used thiourea for the colorimetric determination of tellurium in dusts from lead manufacture.

In the presence of potassium thiocyanate a compound of tellurium and thiourea is extracted from hydrochloric acid solution (0.6–1.7 *N* HCl) by tributyl phosphate[117]. Using an excess of KSCN it is possible to determine very small quantities of tellurium.

III. COMPLEXES OF SELENIUM AND TELLURIUM WITH LIGANDS CONTAINING SULPHUR

1. Complexes of Selenium and Tellurium with Thiosulphate and Its Derivatives

In acidic solutions selenium(IV) and tellurium(IV) are reduced by sodium thiosulphate to selenium(II) and tellurium(II), forming yellow solutions containing the complex ions $[Se(S_2O_3)_2]^{2-}$ or $[Te(S_2O_3)_2]^{2-}$ which are called seleno- or telluro-pentathionate by analogy with pentathionate $[S(S_2O_3)_2]^{2-}$. Selenium and tellurium replace the middle sulphur atom in the pentathionate, forming an unbranched chain –S–S–Te–S–S–.

The pentathionate is formed by the reaction:

$$SeO_2+4Na_2S_2O_3+4HCl=Na_2[Se(S_2O_3)_2]+Na_2S_4O_6+4NaCl+2H_2O.$$

A study of the properties of solutions containing compounds of selenium and tellurium with thiosulphate showed that they are easily decomposed by alkali solutions with separation of elemental selenium and tellurium, but that they are perfectly stable towards acids. Dilute solutions of the compounds can be boiled for some time in the presence of an excess of thiosulphate without fear of decomposition but they decompose slowly in water.

Salts of seleno- and telluro-pentathionic acids were first isolated by Foss[118–120], who obtained the following: $Na_2[Se(S_2O_3)_2].3H_2O$, $Na_2[Te(S_2O_3)_2].2H_2O$, $K_2[Se(S_2O_3)_2].1.5H_2O$, $K_2[Te(S_2O_3)_2]$, $(NH_4)_2[Se(S_2O_3)_2].1.5H_2O$, $(NH_4)_2.[Te(S_2O_3)_2]$, $Rb_2[Se(S_2O_3)_2].1.5H_2O$, $Rb_2[Te(S_2O_3)_2].1.5H_2O$, $Cs_2[Se(S_2O_3)_2]$, and $Cs_2[Te(S_2O_3)_2].1.5H_2O$.

The compounds were isolated as well-formed crystals, the hydrates usually forming more regular crystals. All the compounds are yellow or yellowish green; as a rule, the hydrates are more strongly coloured than the anhydrous compounds. The water molecules in the hydrates are not removed by keeping the substances in a vacuum over sulphuric acid.

The salts which are isolated pure are quite stable and can be kept for some weeks without decomposing. Their solubility in water decreases in the order Na > NH_4 > > K > Rb > Cs, the tellurium salts being somewhat less soluble in water than those of selenium. The Na and NH_4 salts are usually appreciably soluble in methanol and somewhat in 96% ethanol, whereas the K, Rb, and Cs salts are insoluble in alcohols.

Selenopentathionate and telluropentathionate react rapidly and quantitatively with diethyldithiocarbamate to form the compounds $Se[S_2CN(C_2H_5)_2]_2$ and $Te[S_2CN(C_2H_5)_2]_2$.

Examination of the crystal structure of ammonium telluropentathionate $(NH_4)_2[Te(S_2O_3)_2]$ showed[121] that the $[Te(S_2O_3)_2]^{2-}$ ion contains an unbranched –S–S–Te–S–S– chain which has a *trans*-configuration, and the three oxygen atoms are arranged in tetrahedral positions. Hydrogen links

the oxygen atoms and the nitrogen atoms of the ammonium ions.

The thiosulphate complexes of sulphur(II), selenium(II), and tellurium(II) form isomorphous crystals.

Foss synthesised a new type of compound — derivatives of methanethiosulphonate [122,123], $Se(S_2O_2CH_3)_2$ and $Te(S_2O_2CH_3)_2$. These compounds are analogous to the pentathionates, the hydroxy-group of the acid being replaced by methyl.

Telluro- and seleno-bismethanethiosulphonates were obtained as greenish yellow crystals which are insoluble in water, moderately soluble in cold chloroform and ethyl acetate, and insoluble in ether, carbon disulphide, and benzene. The compounds are fairly stable in air and do not change over a period of months. They are decomposed by alkali with separation of elemental sulphur, selenium, and tellurium. Other thiosulphonate derivatives of selenium and tellurium — the bisbenzenethiosulphonate $Te(S_2O_2C_6H_5)_2$ [124,126] and *p*-toluenethiosulphonates [127] — were also obtained. The compounds containing benzene are more stable than those containing *p*-toluene. $Se(S_2O_2C_6H_5)_2$ is fairly readily, and $Te(S_2O_2C_7H_7)_2$ moderately, soluble in warm ethyl acetate, benzene, and chloroform [124].

In these compounds tellurium(II) easily liberates the R-thiosulphonate group in substitution reactions with thiosulphate and diethyldithiocarbamate and forms telluropentathionate and tellurodiethyldithiocarbamate.

Another compound which forms crystals isomorphous with selenium and tellurium sulphonates was obtained; this is the triselenium disulphinate $Se_3(SO_2R)_2$, in which three sulphur atoms have been replaced by three selenium atoms.

Foss [128] also obtained selenium disulphinate $Se(SO_2R)_2$ and diselenium disulphinate $Se_2(SO_2R)_2$, from diselenium dichloride by reaction with an excess of sodium benzenesulphinate and *p*-toluenesulphinate suspended in benzene and ether.

The course of the reaction depends on the nature of the solvent. In benzene mainly diselenium disulphinate is formed,

$$Se_2Cl_2+2RSO_2Na=Se_2(SO_2R)_2+2NaCl,$$

whereas in ether selenium and triselenium disulphinates are produced,

$$2Se_2Cl_2+4RSO_2Na=Se(SO_2R)_2+Se_3(SO_2R)_2+4NaCl.$$

In chloroform containing no ethanol equal amounts of diselenium and triselenium disulphinate are formed.

Crystals of $Se(SO_2C_6H_5)_2$ and $Se(SO_2C_7H_7)_2$ are stable in air, rapidly liberate selenium in sunlight, decompose on heating, are insoluble in water, slightly soluble in warm ligroin, moderately soluble in warm ether, ethanol, and acetic acid, and readily soluble in chloroform, warm benzene, and carbon tetrachloride. Ether solutions of $Se_2(SO_2C_7H_7)_2$ are stable on heating. Solutions of diselenium and triselenium disulphinates in chloroform and ethanol are completely hydrolysed by aqueous alkali. Selenium sulphinates form greenish yellow crystals, the green colour becoming deeper as the number of selenium atoms increases.

Two moles of thiourea can be added to tellurium thiosulphonate to form the mixed compounds $Te(Thio)_2(S_2O_2CH_3)_2$, $Te(Ethio)_2(S_2O_2CH_3)_2$, $Te(Ethio)_2(S_2O_2C_6H_5)_2$, $Te(Tmthio)_2.(S_2O_2CH_3)_2$, and $Te(Tmthio)_2(S_2O_2C_6H_5)_2$. All the compounds isolated are greenish yellow crystals except $Te(Tmthio)_2.(S_2O_2C_6H_5)_2$, which is red. They are completely stable as solids but decompose rapidly in water with liberation of elemental tellurium.

The ability of selenium and tellurium to form thiosulphate complexes is used in a number of titration methods for determining these elements [24,129].

2. Compounds of Selenium and Tellurium with Diethyldithiocarbamate and Its Derivatives

With diethyldithiocarbamate (DDTC) tellurium forms a coloured compound $Te(DDTC)_4$ which is insoluble in water and on extraction passes easily into the layer of organic solvent — chloroform, carbon tetrachloride, etc.[130] Selenium forms a similar compound.

The selenium complex passes quantitatively into the organic phase at pH 4–6.2 but tellurium is extracted over a wider pH range, 4–8.8. The separation of selenium and tellurium carbamates by extraction is usually carried out at pH 8.5–8.7.[131] The presence of complexones in solution, and also of cyanides, citrates, tartrates, phosphates, and borates does not affect the extraction of selenium and tellurium.

The measurement of the optical density of tellurium diethyldithiocarbamate solutions in chloroform is made at 428 mμm,[132–134] the molar extinction coefficient being 3200. Aqueous acetone solutions containing the tellurium compound have an absorption maximum at 340 mμm.[135]

Solutions containing tellurium diethyldithiocarbamate are unstable and are rapidly decolorised, especially in light. Photometry of the solutions must therefore be carried out immediately after development of the colour, using a vessel made of dark glass.

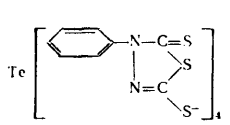
Determination of tellurium with diethyldithiocarbamate is used in the analysis of iron and steels [136], pure selenium [137], platinum metals [138], and lead and copper [92].

Sodium 3,5-diphenylpyrazoline-1-dithiocarbamate forms a yellow compound with tellurium, which is readily soluble in chloroform and carbon tetrachloride and is more stable than tellurium diethyldithiocarbamate in solutions in organic solvents.

The compound of tellurium with 3,5-diphenylpyrazoline-1-dithiocarbamate is extracted by chloroform over a wide acidity range — from 12 *N* HCl to pH 9. The absorption spectrum of solutions in chloroform has a maximum at 415 mμm and the apparent molar extinction coefficient is 20 400 at this wavelength [139].

3. Compounds of Tellurium with Bismuthol-II (Mercaptophenylthiolthiadiazolone)

With tellurium, Bismuthol-II forms a coloured compound



which is insoluble in water but passes easily into an organic phase; at pH 5–8 it is extracted by alcohols, ketones, chloroform, and carbon tetrachloride. The extraction reaches a maximum at pH 3.3–4.3.[3]

Quantitative formation of the compound in aqueous solution is observed at pH 2.0–2.2.[4] At pH 8 the compound decomposes. A complex of selenium with Bismuthol-II is formed at a higher acidity.

The colour of solutions of the tellurium compound in organic solvents is stable on standing and has an absorption maximum at 335 mμm, but quantitative measurements are made at 415 mμm, where the absorption of the reagent is minimal. At this wavelength the molar extinction coefficient is 28 000.

Bismuthol-II is used to determine traces of tellurium in ores and in pyrites[3] and to determine tellurium in cadmium and mercury tellurides[140].

IV. OTHER COMPLEXES OF SELENIUM AND TELLURIUM

Nickel diethyldithiophosphate reacts[141,142] with selenous acid to form a yellowish amorphous precipitate of $[(C_2H_5O)_2PSS]_2Se$. Selenium(II) diethyldithiophosphate is quite stable, is insoluble in water, but dissolves readily in organic solvents (chloroform, carbon tetrachloride, benzene, etc.) forming coloured solutions with an absorption maximum at 315–320 mμm. However, the disulphide absorbs considerably in this region, so that this reaction cannot be used for the quantitative determination of selenium.

When a solution of $TeCl_4$ in benzene reacts with dicarboxylic acids[143] the following compounds are formed: $[(CH_2)_2(COO)_2]_2Te$ with succinic acid, $[(CH_2)_4(COO)_2]_2Te$ with adipic acid, and $[C_6H_4(COO)_2]_2Te$ with phthalic acid.

Hydroxy-acids (salicylic, gallic, tannic, malonic) form the following compounds with tellurium:

$$(HOC_6H_4COO)_4Te, \quad [(HO)_3C_6H_2COO]_4Te,$$
$$(C_{14}H_8O_9)_2Te, \quad [CH_2.CHOH.(COO)_2]_2Te.$$

All the substances isolated are soluble in ethanol, acetone, and ethylacetone [ethyl acetate? (Ed. of Translation)], but insoluble in ether, chloroform, and carbon tetrachloride.

Tellurium forms heteropolyacids in which tellurium(IV) or tellurium(VI) can be the central atom. Rosenheim and Traube[144] obtained heteropoly compounds of tellurium(VI) of the type $R_6[Te(WO_3)_6]$, where R = Na, K, NH_4, or guanidinium.

Ganelina[145] synthesised the tetrabasic dodecatungstotelluric acid $H_4[TeO_4(H_2WO_4)_{12}].13H_2O$, which is a yellow crystalline powder, readily soluble in water. Aqueous solutions of the heteropolyacid are not decomposed by concentrated sulphuric acid. In hydrochloric acid solution the heteropolyanion $[TeO_4(H_2WO_4)_{12}]^{4-}$ is stable at an HCl concentration less than 1.138 *N*.

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tensive programme for the production of mineral fertilisers, weed-killers, chemical poisons, and other crop-protecting substances, in order to fulfil the country's economical requirements. It has been estimated that by 1970 the agricultural needs will amount to 70–80 million tonnes of mineral fertilisers, 800–900 thousand tonnes of insecticides, fungicides, and weed-killers. To meet these goals in the production of fertilisers the capacity of the existing plants must be increased by about 20 million tons and 55 new plants must be built, of which 28 are for nitrogeneous fertilisers, 19 for phosphate fertiliers, 6 are potash mines and 2 are for production of phosphate meal [19 for superphosphate and 2 for bone meal ? (Ed. of Translation)].

These goals will be achieved by speeding up the construction of new plants, as well as workshops and individual production units at existing factories. In addition to the increased volume of production of fertilisers and chemical poisons for agricultural purposes their quality and range must also be improved.

At the moment a considerable proportion of the fertilisers supplied to agricultural undertakings are inadequate in terms of nutrient components; for example, of the potassium fertilisers about one-half are crude potassium salts. The situation is similar in the case of phosphate fertilisers.

In future the new plants will be producing mainly highly concentrated mixed fertilisers to enrich the soil with all the necessary nutrient substances in the required amounts and proportions.

The development of agricultural chemistry gives rise to new scientific problems, requiring profound and systematic research into the synthesis of the most effective mineral fertilisers, especially highly concentrated and complex ones, development of economical methods for their manufacture, production of optimal mixtures of fertilisers for the main soil and climatic zones and the most important crops, as well as the production of new effective agents against weeds, pests, and crop diseases.

The Plenary Session has also outlined a comprehensive programme for the development of the manufacture of clothing, footwear, and other consumer goods based on products of the chemical industry. The target production of synthetic fibres for 1970 is 1.35 million tonnes. This will serve as a basis for qualitative changes in the textile industry, with a changeover to extensive production of knitted fabrics, artificial leather goods and non-woven fabrics, with consequent improvement in the quality of the goods, greater efficiency of production and reduction of cost.

The target production of plastics and synthetic resins for 1970 is 3.5–4 million tonnes.

Plastics should largely replace non-ferrous metals whenever it is economically and technologically possible; they should also be widely used for the manufacture of machine components and pipes, and for treating wood, especially for floor coverings, finishing materials, sanitary-technical equipment, etc.

An important goal put forward by the Plenary Session is the organisation of full-value replacements of raw food materials so that by 1967–1968 no grain, sugar, vegetable oils, or other foodstuffs will be used for technological purposes.

Among the tasks of the fine chemicals industry, also considered by the December Plenary Session, are the creation of a pure reagents industry and production of super-purity metals and various equipment needed for further scientific and industrial developments.

An extensive development of theoretical and applied chemical research has been outlined for Soviet science.

Having directed the work of scientific research organisations towards the creation of new materials and the development of more suitable, simple, and economical technological processes, the Plenary Session of the Central Committee of the Soviet Communist Party paid particular attention to the need for completing promptly the development of production methods, of more effective fertilisers and chemical pesticides for crops, new plastics, synthetic fibres, synthetic rubbers, dyestuffs, lacquers, pigments, and other chemical products.

Special stress was laid on the need to ensure rapid incorporation of scientific advances into industry and to attain the highest technological levels in the chemical industry.

It is also most important to develop the fundamentals of chemical technology and to create methods of small-scale testing and calculating technological processes with the help of computers.

The programme for the rapid development of the chemical industry, agriculture, and light industry adopted by the December Plenary Session is of the utmost national importance, with enormous bearing upon communist construction, economic development and reinforcement of the country's might.

The rewarding task of all workers in chemical science and industry is the creative and prompt fulfilment of all the goals of the development of chemical science and the incorporation of chemistry into the national economy.

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ADDITION OF ALCOHOLS AND MERCAPTANS TO COMPOUNDS WITH TRIPLE BONDS

M. F. Shostakovskii, A. V. Bogdanova, and G. I. Plotnikova

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I. INTRODUCTION

Reactions involving the addition of alcohols and mercaptans to acetylenes have been known for a long time. Investigation of the conditions in which these reactions take place led to the development of a method of vinylating alcohols and mercaptans and the preparation of vinyl ethers and sulphides. Apart from acetylene, its various monosubstituted derivatives have been used as vinylating agents.

In recent years many studies have been made on the reaction of diacetylene with various compounds containing reactive hydrogen, including alcohols and mercaptans, which led to the synthesis of ethynyl vinyl and butadienyl ethers and sulphides.

The increasing interest of organic chemists in diacetylene has arisen because this compound is formed as a side-product in the preparation of acetylene by thermal cracking of natural gas; its utilisation as a new starting material is thus one of the urgent problems of synthetic chemistry. The available literature data on the addition of alcohols and mercaptans to compounds containing a triple bond have not been surveyed so far, which makes it difficult to become familiar with the investigations which have been made in the field of acetylene derivatives, and in particular diacetylene. We therefore felt it was timely to review studies dealing with additions of alcohols and mercaptans to acetylenes, diacetylenes, and some of their derivatives.

II. ADDITION OF ALCOHOLS AND MERCAPTANS TO ACETYLENES

1. Addition of Alcohols to Acetylene

In his study of the isomerisation of substituted acetylenes on heating with alcoholic alkali, Favorskii[1] showed that alcohols add on to substituted acetylenes, forming vinyl ethers. A synthesis of vinyl ethers by vinylating acetylene with alcohols was developed on the basis of this reaction[2,3].

At present this is the principal industrial method of manufacturing a wide variety of vinyl ethers in the USSR. The vinylation of alcohols with acetylene is carried out in an autoclave under pressure, at elevated temperatures, and in the presence of strongly alkaline catalysts. In recent years this reaction has been extended to many different alcohols, phenols, naphthols, and other compounds containing reactive hydrogen[3,4].

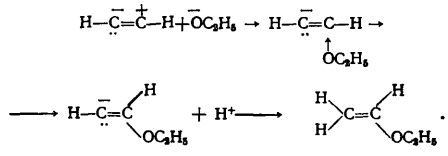
It is noteworthy that in the vinylation of alcohols and phenols some investigators[4] have used acetylene diluted with nitrogen, which in their view prevented explosions and did not interfere with the main reaction. However, Shostakovskii and coworkers[3] showed that dilution of acetylene with nitrogen is not necessary and in many cases slows down the reaction and necessitates an increase in temperature, which gives rise to side-reactions.

The rate of vinylation significantly depends on the structure of the initial alcohol. Holly[5] found that it falls sharply on going from a primary to a tertiary alcohol. For example, in the vinylation of secondary and tertiary alcohols it is necessary to use potassium alkoxides, and not inorganic alkali which causes resinification of the products.

Phenols, cresols, and naphthols are vinylated under more severe conditions than aliphatic alcohols: a larger amount of alkali, the presence of water, and a higher temperature are necessary, probably because of the acidic properties of phenols. Alizarin, for example, has pronounced acidic properties and is not vinylated under the usual conditions[6].

Optimum conditions have been found for the preparation in good yield of vinyl phenyl, vinyl cyclohexyl, vinyl 2-decalyl, and vinyl 2-naphthyl ethers[7-9]. The vinylation of phenols requires the presence of a large amount of water which prevents the thermal polymerisation of the vinyl ethers[8] and favours the formation of phenoxide ions which accelerate the vinylation[10]. The role of water as a factor favouring the ionisation of phenols during their vinylation has also been considered by Ban *et al.*[11], who confirmed that the reaction depends on the concentration of the $C_6H_5O^-$ ions. They investigated in detail the pH of the medium required for the vinylation of phenols, cresols, and *p*-nitrophenol in aqueous solutions in the presence of alkali, and found that the nature of the alkaline reagent does not affect the rate of reaction provided that the optimum pH is maintained; the reaction does not take place in the absence of alkali. On this basis, they believe, together with Reppe[4] and Miller[10,12], that vinylation of alcohols is a nucleophilic addition reaction.

In view of the electrophilic activity of the triple bond, Müller put forward the following mechanism[13]:



Among recent investigations dealing with the kinetics of vinylation of various alcohols with acetylene in the presence of metal alkoxides are those of Japanese workers[14,15], who proposed a mechanism for this reaction, involving the formation of an intermediate complex of the alcohol, alkoxide, and acetylene, which then breaks down and KOH is liberated under the reaction conditions. However, these workers say nothing about the nature of these complexes.

2. Addition of Mercaptans to Acetylene

Syntheses based on acetylene and mercaptans were first described by Reppe[4,16] in a number of patents, which showed that aliphatic, aromatic, and hydroaromatic mercaptans are vinylated under conditions similar to those

used in the vinylation of alcohols and phenols, the reaction resulting in the formation of the corresponding vinyl sulphides, which can be isolated in good yields[17]:

$$CH{\equiv}CH+RSH \longrightarrow CH_2{=}CH{-}SR.$$

Thus in the reaction with acetylene diluted with nitrogen (2 : 1) in the presence of butanol and solid KOH at 160°, thiophenol is almost quantitatively converted into vinyl phenyl sulphide in 12 h. In the vinylation of mercaptans, as in the case of alcohols, Reppe used nitrogen, which in the view of Shostakovskii *et al.*[18-23] hinders the reaction.

According to Reppe[4], the reaction of mercaptans with acetylenes takes place as follows:

$$RSH+KOH \longrightarrow RSK+H_2O$$

$$RSK \xrightarrow{CH{\equiv}CH} [RS{-}CH{=}CHK] \xrightarrow{RSH} RS{-}CH{=}CH_2+RSK.$$

Later, this reaction was studied in detail by Shostakovskii and coworkers[18-24], who found optimum conditions for the preparation of vinyl sulphides of different structures. They observed that such conditions for this reaction depend on the structure of the initial mercaptan, and investigated the effect of temperature, catalyst concentration, and various solvents and diluents on the course of the reaction. Particular attention was paid to inhibiting the secondary reaction between the vinyl sulphide formed and the mercaptan, which under the reaction conditions shows anti-Markovnikov addition:

$$RS{-}CH{=}CH_2+RSH \longrightarrow RS{-}CH_2CH_2SR.$$

They showed[21] that a good yield of vinyl sulphide may be obtained in the presence of an excess of acetylene, and recommended dioxan[20], methanol, butanol, formals[25], etc., as solvents. Apart from these, Schneider[26] used aqueous solutions of weak bases for the preparation of vinyl thioethers. Alcohols may be used as solvents in the synthesis of vinyl sulphides because mercaptans are much more readily vinylated.

The higher activity of the mercapto-group compared with the hydroxyl in the vinylation reaction is well illustrated by the reaction of monothioethylene glycol with acetylene[22], which involves only the mercapto-group and results in the formation of 2-hydroxyethyl vinyl sulphide:

$$HO{-}CH_2{-}CH_2{-}SH+CH{\equiv}CH \longrightarrow HO{-}CH_2{-}CH_2{-}S{-}CH{=}CH_2.$$

Phenylacetylene undergoes an exothermic reaction with mercaptoethanol in the presence of catalytic amounts of alkali and here too only the mercapto-group is involved[27]:

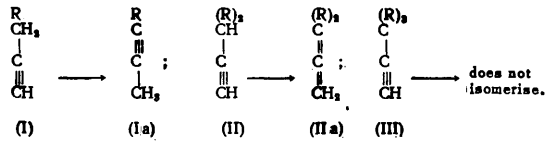
$$C_6H_5C{\equiv}CH+HS{-}CH_2{-}CH_2{-}OH \longrightarrow C_6H_5{-}CH{=}CH{-}S{-}CH_2{-}CH_2{-}OH.$$

Comparison of the conditions for the addition of alcohols and mercaptans to acetylene shows that in general they are similar for both types of reaction. However, the reaction of mercaptans with acetylene is not confined to the addition of one mercaptan molecule, so that the reaction mixture always contains a considerable amount of 1,2-alkylthioethanes. The reaction of acetylene with mercaptans in the presence of free-radical initiators at 130° at a pressure of 13–17 atm in an autoclave has been described in a recent communication[28]. It is suggested that the alkylthio- or arylthio-radical RS$^{\cdot}$ adds on to the acetylene molecule with the formation of a new double-bonded radical, RS–CH=$\dot{C}$H. This radical is stabilised by reaction with a mercaptan molecule, in which the alkylthio-radical is liberated, etc:

$$RS{-}CH{=}\dot{C}H+RSH \longrightarrow RS{-}CH{=}CH_2+RS^{\cdot}.$$

3. Addition of Alcohols to Substituted Acetylenes

The addition of alcohols to substituted acetylenes was first investigated by Favorskii[1] and described in his series of papers on the mechanism of isomerisation of hydrocarbons. Investigating the reaction of various substituted acetylenes (I), (II), and (III) with alcoholic alkali, Favorskii found that monosubstituted acetylenes (I) are then isomerised to disubstituted acetylenes (Ia), disubstituted acetylenes (II) are isomerised to allenes (IIa), whereas acetylene with a tertiary substituent (III) does not isomerise under these conditions.



(I) (Ia) (II) (IIa) (III)

Favorskii[1] also discovered that reaction of methylacetylene with alcoholic potassium hydroxide results in the formation of ethyl isopropenyl ether:

$$CH_3{-}C{\equiv}CH+C_2H_5OH \longrightarrow CH_3{-}\underset{\displaystyle OC_2H_5}{\underset{|}{C}}{=}CH_2.$$

and noted that the reaction involved the isomerisation of methylacetylene to allene:

$$CH_3{-}C{\equiv}CH \rightleftarrows CH_2{=}C{=}CH_2.$$

Shostakovskii *et al.*[29-34] investigated in detail the conditions of the reaction of methylacetylene with other alcohols and phenols, paying particular attention to the equilibrium between methylacetylene and allene. They made a special study of the behaviour of allene under the conditions of this reaction and found that allene, without even a trace of methylacetylene, isomerises almost quantitatively at 200° in 50% potassium hydroxide solution to methylacetylene, which was isolated as the acetylide. Frank-Kamenetskii and Markovich[35] established that at 200° this equilibrium is displaced towards methylacetylene to the extent of 90%.

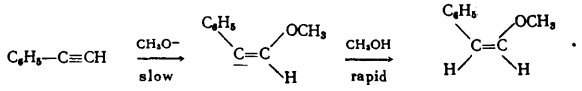
On the basis of this finding and their own experimental results, Shostakovskii *et al.*[29] showed that this temperature is most favourable for the synthesis of isopropenyl ethers from alcohols and methylacetylene. Furthermore, they found that allene or its mixture with methylacetylene can also be used for vinylation. Using various alcohols and phenols, they synthesised different α-substituted vinyl ethers[30-33] and noted that the reaction of alcohols with methylacetylene requires more severe conditions than that with acetylene.

Reactions involving addition of alcohols to substituted acetylenes containing electron-acceptor groups are particularly interesting[36]. In contrast to alkyl-substituted acetylenes such as methylacetylene, in this case the alkoxy-group of the alcohol adds to the β-carbon atom of the substituted acetylene. Thus phenylacetylene readily reacts

with different alcohols in the presence of alkali at 130–140°, forming the corresponding β-alkoxystyrenes which can be isolated in good yield[10,12,37,38]:

$$R'-C\equiv CH+ROH \longrightarrow R'-CH=CH-OR.$$

According to Miller and Shapenko[12], this too is an ionic nucleophilic reaction which can take place stereospecifically with formation of the *cis*-isomer:



Nitrophenylacetylenes add to alcohols by this mechanism even more vigorously[39]:

$$p\text{-}NO_2C_6H_4-C\equiv CH+ROH \longrightarrow p\text{-}NO_2C_6H_4-CH=CH-OR.$$

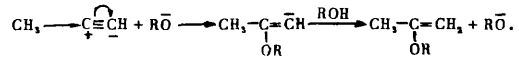
Another substituted acetylene of this type is trifluoromethylacetylene which undergoes an exothermic reaction with ethanol in an alkaline medium[36]:

$$CF_3-C\equiv CH+C_2H_5OH \xrightarrow{C_2H_5ONa} CF_3-CH=CH-OC_2H_5.$$

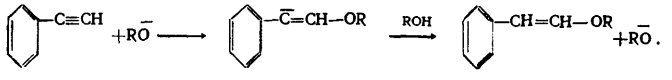
Alcohol adds similarly to the triple bond of the acetal of propiolaldehyde[40]:

$$CH\equiv C-CH(OC_2H_5)_2+C_2H_5OH \xrightarrow{C_2H_5ONa} C_2H_5O-CH=CH-CH(OC_2H_5)_2.$$

The presence of a substituent in the acetylene molecule polarises the triple bond in a way which depends on the electronic properties of the substituent. Electron-donor substituents displace the electrons, thereby polarising the molecule, in such a way that addition of an alkoxide ion to the α-carbon atom is favoured[29]:



Electron-acceptor substituents, on the other hand, polarise the triple bond in the opposite sense, which results in the addition of an alkoxide ion to the β-carbon atom:

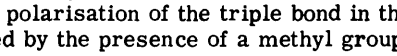


All the above applies to the addition of alcohols to monosubstituted acetylenes, *i.e.* to acetylenes having a reactive hydrogen atom. However, it is known that alcohols can also add to disubstituted acetylenes, which do not have a reactive hydrogen atom; for example, an alcohol can add on to tetrolic acid and acetals of tetrolaldehyde in an alkaline medium with formation of an unsaturated acid[41].

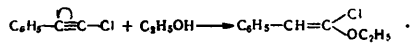
In an alkaline or acid medium in the presence of $HgSO_4$ an alcohol molecule can add to the dibutyl acetal of tetrolaldehyde with formation of an unsaturated ether-acetal:

$$CH_3-C\equiv C-CH(OR)_2+ROH \longrightarrow CH_3-C(OR)=CH-CH(OR)_2.$$

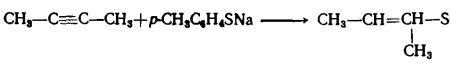
The mechanism of this reaction is probably similar to that of the nucleophilic addition of alcohols to monosubstituted acetylenes. Tetrolic acid has a carboxy-group which lowers the electron density at the triple carbon–carbon bonds thus making possible the addition of an alcohol molecule. The polarisation of the triple bond in this direction is facilitated by the presence of a methyl group:



For this reason, the absence of a reactive acetylenic hydrogen in 1-chloro-2-phenylacetylene does not prevent the addition of alcohol in an alkaline medium with formation of β-chloro-β-ethoxystyrene[42]:



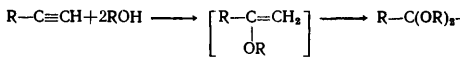
However, addition to the triple bond does not depend solely on the electronic properties of the adjacent substituents. The nature of the adding molecule has a considerable influence on the reaction. Powerful nucleophilic reagents, for example mercaptans, can add, in an alkaline medium, to disubstituted acetylenes without electron-acceptor substituents. The sodium salt of *p*-thiocresol readily adds on to but-2-yne[43]:



The rate of addition to the triple bond depends on how nucleophilic is the attacking ion[44], this property decreasing in the series[45]

$$\bar{S}Alk > \bar{O}Alk > \bar{O}Ar.$$

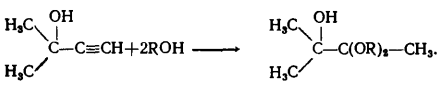
The reactions involving addition to various substituted acetylenes described above were carried out in the presence of alkaline catalysts. However, they have also been investigated under conditions of acid catalysis. Nieuwland and coworkers[46] showed that straight-chain primary alcohols add smoothly to acetylenic hydrocarbons, under the action of boron trifluoride and mercuric oxide, with formation of ketals, which can be isolated in high yields:



Under these conditions three molecules of alcohol add to vinylacetylene forming 1.3,3-trialkoxybutanes[47]:

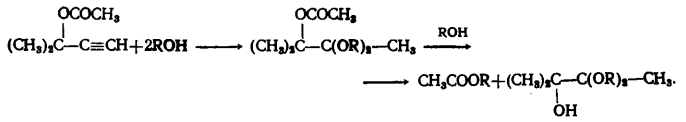
$$CH_2=CH-C\equiv CH+3ROH \longrightarrow RO-CH_2CH_2-C(OR)_2-CH_3.$$

These reactions involve a stage in which α-substituted vinyl ethers, which were not isolated, are formed. Nazarov[48] investigated in detail and described the addition of aliphatic alcohols to a tertiary ethynyl alcohol — ethynyldimethylmethanol. This addition takes place smoothly with formation of the ketal of acetyldimethylmethanol in 60–80% yield and also involves a stage in which the α-substituted vinyl ether is formed:

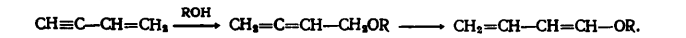


In the presence of BF_3 and HgO three molecules of methanol add to 1,1-dimethylprop-2-ynyl acetate and the latter is quantitatively converted into methyl acetate and

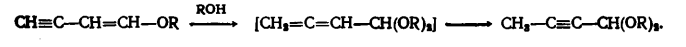
the ketal of acetyldimethylmethanol. The reaction involves two stages:



Among the compounds with the triple bond considered here, vinylacetylene occupies a special place because its multiple bonds are strongly conjugated, which according to Petrov [49] to a large extent determines the mode of the addition reactions. In a detailed review dealing with vinylacetylene and its homologues, Petrov interprets the reaction with alcohol as addition to the conjugated vinylacetylene system. In the presence of potassium alkoxide at the normal pressure alcohols undergo 1,4-addition with formation of 1-alkoxybutadienes, as a result of the subsequent allene-1,3-diene isomerisation [49,50]:



A molecule of alcohol adds to ethynyl vinyl ether on heating in the presence of alkali, acetals of but-2-yn-4-al being formed [51-53]:

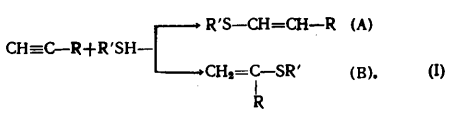


It appears that the 1,4-addition of the alcohol occurs as in the case of vinylacetylene.

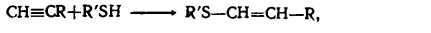
4. Addition of Mercaptans to Substituted Acetylenes

Most of the detailed investigations of the addition of mercaptans to substituted acetylenes have been made in the last decade, those of Truce and coworkers [43,54,55] being particularly important. Apart from its practical importance (this reaction serves as a basis for the development of a method of synthesing a wide variety of unsaturated sulphides), it is also of considerable theoretical interest. It made it possible to investigate the variation in the properties of the triple bond with the nature of the substituents in the acetylene, the influence of the mercaptan which adds on, and the influence of the mechanism on the mode of the reaction. Furthermore, by investigating the stereochemistry of the addition of mercaptans to substituted acetylenes, Truce and coworkers were able to find the conditions under which this reaction is stereospecific, to observe some of the rules governing it, and to formulate the so-called "rule of *trans*-nucleophilic addition" which is general for substituted acetylenes [55].

Depending on the reaction conditions, the addition of mercaptans to substituted acetylenes can take place differently, resulting in the formation of α- or β-substituted vinyl sulphides:

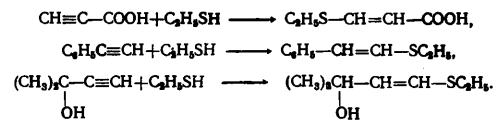


Truce and coworkers [43,54-60] showed that reactions with mercaptans and acetylenes having electron-acceptor substituents result in the formation of β-substituted vinyl sulphides, which were isolated in good yields:

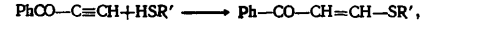


where R = C_6H_5, Cl, p-$CH_3C_6H_4$, COC_6H_5, COC_2H_5, or COOH, and R′ = p-$CH_3C_6H_4$, CH_3, C_6H_5, or mesityl. The reaction takes place when an alcoholic alkaline solution of acetylene and the mercaptan is boiled for 15–23 h. Truce and coworkers found that in some cases the reaction can occur in two ways, (A) and (B), for example, in the case of butylacetylene and p-thiocresol [56].

Other workers, who investigated the free-radical addition of mercaptans to acetylenes with electron-acceptor substituents, discovered that this too results in β-substituted vinyl sulphides. Thus Kohler and Potter [61] found that thiocresol undergoes an exothermic reaction with phenylacetylene forming 1-phenyl-2-tolylthioethylene which was isolated in quantitative yield. Blomquist and Wolinsky [62] showed that in the presence of benzoyl peroxide and on irradiation with ultraviolet light ethanethiol yields β-substituted vinyl sulphides when it reacts with phenylacetylene, propiolic acid, and 2-methylbut-3-yn-2-ol:

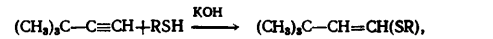


Ethynyl ketones [63], to which mercaptans add quantitatively with formation of β-substituted vinyl sulphides, can also be regarded as acetylenes with electron-acceptor substituents:



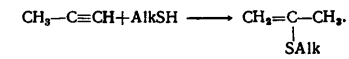
where R′ = Ph or C_2H_5.

Shostakovskii *et al.* [64] investigated the addition of mercaptans to t-butylacetylene in the presence of alkali, and discovered that the reaction also results in the formation of β-substituted vinyl sulphides:



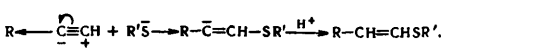
where R = C_2H_5, C_3H_7, or C_4H_9. According to these workers, this course of reaction can be explained either by steric hindrance due to the t-butyl group in the acetylene or by a radical mechanism of the process, since the reaction was carried out in an autoclave in the presence of atmospheric oxygen.

Addition of mercaptans to acetylene with electron-donor substituents yields α-substituted vinyl sulphides, *i.e.* the reaction is similar to the addition of alcohols [29] to these acetylenes. Shostakovskii *et al.* [65,66] studied the conditions of the reaction of methylacetylene and mercaptans in an alkaline medium and found that in the reaction with alkanethiols isopropenyl alkyl sulphide is the main reaction product:

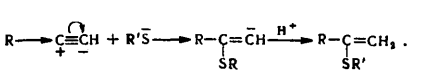


The addition of thiophenol to methylacetylene under these conditions results in the formation of two compounds, isopropenyl phenyl and propenyl phenyl sulphides, according to reactions (A) and (B). Shostakovskii *et al.* [66] were unable to suppress reaction (A) even in the presence of hydroquinone in the medium. On the basis of this reaction, they developed a method of synthesing isopropenyl alkyl (aryl) sulphides (temperature 120–170° depending on the mercaptan, elevated pressure, and alkaline medium).

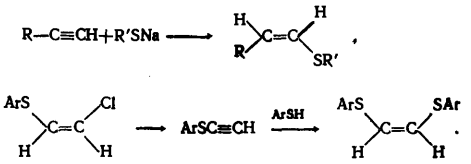
It may be assumed that the activation of the triple bond in this reaction results from the displacement of the electrons towards the electron-donor substituent, which facilitates nucleophilic attack on the triple bond:



In the case of an electron-acceptor substituent, the electrons are displaced in the opposite direction, and α-substituted vinyl sulphides are formed:



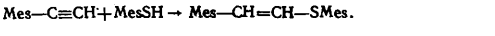
Truce and coworkers [43,54-60] and Montanari [67-69] investigated the stereochemistry of the addition of mercaptans to acetylenes having different electronegative substituents. In their study of the addition of mercaptans to phenylacetylene, but-2-yne, chloroacetylene, and *p*-toluenesulphonylmesitylthioacetylene as examples they discovered [43,44,55] that the addition results in the formation of *cis*-isomers in 73–79% yield:



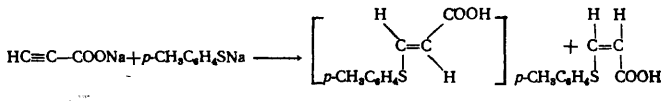
On the basis of a detailed examination of the reaction conditions, Truce and coworkers [43,54,57] concluded that the reaction of mercaptans with monosubstituted acetylenes having electronegative groups takes place stereospecifically under ionic conditions and obeys the *trans*-nucleophilic addition rule. In the view of these workers [43,57], the addition involves a stage in which an intermediate carbanion is formed:

From a comparison of the results of these investigations, Truce [57] concluded that the formation of *cis*-products is the result of both electronic and steric factors.

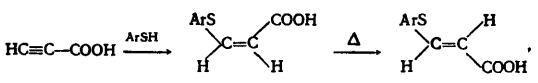
Attempts to circumvent the *trans*-nucleophilic addition rule by introducing the bulky mesityl group into acetylene and then adding to the product 2,4,6-trimethylbenzenethiol in an alkaline medium were unsuccessful [57]. *cis*-1-Mesityl-2-mesitylthioethylene was isolated as the principal product:



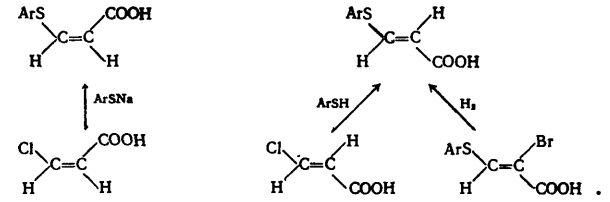
Truce and coworkers [54-57] thought that they had found a partial exception from the nucleophilic addition rule in the addition of *p*-thiocresol to sodium propiolate, but Montanari and coworkers [67-69] showed that this conclusion was erroneous:



The Italian workers [67-69] were the first to prepare *cis*- and *trans*-β-arylthioacrylic acids in different ways: by the reaction of thiophenol with propiolic acid



by nucleophilic substitution of the chlorine by arylthio-groups in *cis*- and *trans*-β-chloroacrylic acid, and by the reduction of *trans*-β-arylthio-α-bromoacrylic acid



The structure of the isomers was confirmed by infrared spectroscopy, reduction, isomerisation, nuclear magnetic resonance, and by the investigation of the analogous *cis*- and *trans*-isomers of acids derived from the corresponding chloroacrylic acids.

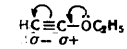
On the basis of a study of the reactivity of the triple bond in acetylene derivatives containing negatively charged groups in nucleophilic addition reactions, Truce and coworkers [58] arranged the substituents in the following sequence:

III. ADDITION OF ALCOHOLS AND MERCAPTANS TO ETHYNYL ETHERS AND SULPHIDES

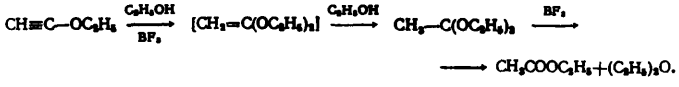
Ethynyl ethers and sulphides with the general formula CH≡C–OR(SR) may be regarded as monosubstituted acetylenes. It is interesting to investigate the reactivity of the triple bond in these compounds as a function of the nature of the heteroatom and the R radical.

1. Addition of Alcohols to Ethynyl Ethers and Sulphides

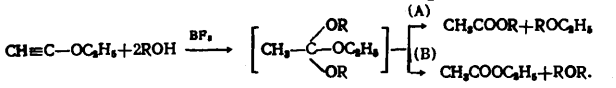
The effect of the nature of substituents adjacent to a multiple bond on its polarisation and consequent mode of reaction were discussed above. The direction of polarisation in ethynyl ethers may be represented as follows:



Arens and coworkers [70], who investigated the behaviour of ethynyl ethers and sulphides in electrophilic and nucleophilic addition reactions adopted this mechanism. In his investigation of the addition of alcohols and phenols to ethoxyacetylene, Arens found that this reaction is greatly facilitated by the presence of BF_3 in the reaction mixture [70-72]. He represents the addition of ethanol to ethoxyacetylene as follows:



If instead of ethanol other alcohols are used in the reaction, a mixed orthoester is formed and can break down into ester and ether molecules containing different radicals:



Since the acetate and the ethyl ether of the given alcohol (or phenol) are the main reaction products the above investigators believe reaction (A) to be the main one. The addition of alcohol to ethoxyhept-1-yne in the presence of boron trifluoride and mercuric oxide has also been investigated. The reaction takes place at room temperature and results in the formation of ethyl heptanoate [73]:

$$C_6H_{11}-C\equiv C-OC_2H_5+2C_2H_5OH \longrightarrow [C_6H_{11}-CH_2-C(OC_2H_5)_3] \xrightarrow[HOH]{BF_3\cdot HgO} C_6H_{11}CH_2-COOC_2H_5+2C_2H_5OH.$$

In earlier investigations [72,74] it was shown that alcohols can add to ethoxyacetylene also under the influence of their alkoxides. However, this reaction is slower than in the presence of acid reagents and terminates in the formation of the ortho-ester which does not decompose under conditions of alkaline catalysis:

$$CH\equiv C-OC_2H_5 \xrightarrow{C_2H_5O^-} [CH=C(OC_2H_5)_2] \xrightarrow{H^+} CH_2=C(OC_2H_5)_2 \xrightarrow{C_2H_5OH} CH_3-C(OC_2H_5)_3.$$

Arens [70] therefore regards the alkoxide-catalysed addition of an alcohol to ethoxyacetylene as nucleophilic addition of the alkoxide ion to the α-carbon atom of the ether, followed by scission and addition of a proton. The final stage is addition of yet another alcohol molecule.

The electron-donor properties of ethoxy-groups in ethynyl ethers are also shown in electrophilic addition reactions. For example, in the reaction of water with ethoxyacetylene [70,74,75], the latter can be hydrated under the influence of both acid (mineral acids) and alkaline catalysts. Arens [75] regards the base-catalysed addition of water to ethoxyacetylene as nucleophilic addition. These studies show that nucleophilic and electrophilic addition reactions of ethynyl ethers are due to the electron-donor properties of the OR groups and take place more readily under the influence of acid catalysts.

Ethylthioacetylene behaves quite differently in electrophilic and nucleophilic additions to the triple bond. Thus, in contrast to the very rapid hydration of ethoxyacetylene in the presence of acid, the corresponding reaction with ethylthioacetylene is very slow and its completion requires prolonged boiling [70], the principal products being acetic acid and the mercaptan:

$$CH\equiv C-SC_2H_5 + H^+ \longrightarrow CH_2=\overset{+}{C}-SC_2H_5 \xrightarrow{H_2O} CH_3-\underset{\underset{O}{\|}}{C}-SC_2H_5 + H^+$$

$$\xrightarrow[H_2O]{H^+} CH_3COOH + C_2H_5SH.$$

In terms of Ingold's theoretical ideas [76], Arens [70] expressed this by saying that the "conjugative displacement" of electrons from the RS group in ethylthioacetylene takes place in the same direction as in ethoxyacetylene but to a much lesser extent, and therefore the hydration is more difficult.

Arens [75] showed that, in contrast to the electrophilic reactions of ethylthioacetylene, its nucleophilic additions (even those involving alcohols) do not cause polarisation of the triple bond in the manner characteristic of ethoxyacetylene. Nucleophilic groups always add at the β-carbon atom of ethylthioacetylene, which shows that the latter is polarised as follows [70,75]:

$$HC\overset{\delta-}{\equiv}C\overset{\delta+}{-}SC_2H_5.$$

Addition of alcohols and phenols to ethyl sulphides takes place in the presence of alkoxides [77,78], this process also being slow. On being boiled with sodium ethoxide for 7 h in a stream of nitrogen, ethylthioacetylene forms *cis*- and *trans*-1,2-substituted ethylenes in good yield [77]:

$$CH\equiv C-SC_2H_5+C_2H_5ONa \longrightarrow C_2H_5O-CH=CH-SC_2H_5.$$

The addition of sodium ethoxide to ethylthiopropyne takes place on heating the mixture to 140° for 24 h, the β-adduct being formed in good yield [78]:

$$CH_3-C\equiv C-SC_2H_5+C_2H_5ONa \longrightarrow CH_3-C(OC_2H_5)=CH-SC_2H_5.$$

On the basis of the experimental data, Volger and Arens [70,75] concluded that the alkylthio-group has a twofold effect on the polarisation of the adjacent triple bond, by virtue of the capacity of sulphur to adapt readily to the electronic requirement of the approaching group. This behaviour of the alkylthio-group and its consequent influence on the polarisation of the neighbouring triple bond arises from the capacity of sulphur in the alkylthio-group to extend its octet of valence electrons to ten or to give them up [70].

In contrast to alkylthio-groups, which can behave both as electron donors and acceptors, alkoxy-groups in ethynyl ethers exhibit only electron-donor properties in the above reactions, polarising the molecule only in the following way:

$$CH\overset{\delta-}{\equiv}C\overset{\delta+}{-}OC_2H_5.$$

2. Addition of Mercaptans to Ethynyl Ethers and Sulphides

Mercaptans react with ethynyl ethers and sulphides by a free-radical mechanism, β-substituted products being formed [70,75]:

$$CH\equiv C-OR(SR)+R'SH \longrightarrow R'S-CH=CH-OR(SR).$$

Arens and coworkers [79] showed that mercaptans readily add to ethoxy- and ethylthio-acetylene when the mixture is heated slightly. According to Arens [70], the mechanism of this reaction involves the formation of an intermediate radical $C_2H_5S-CH=\dot{C}-OC_2H_5(SC_2H_5)$, the orientation of the molecule during the reaction being determined by the approaching SC_2H_5 group and the relative stability of the radical.

The reaction of ethanethiol with ethoxy- and ethylthio-acetylene results in a mixture of *cis*- and *trans*-isomers of 1,2-disubstituted ethylenes. An experiment carried out under conditions excluding the possibility of isomerisation yielded only the *cis*-isomer, which was converted into the *trans*-isomer on distillation. Arens and coworkers [79] concluded from these results that the addition of ethanethiol to ethynyl ethers and sulphides is stereospecific and takes place in accordance with the "*trans*-addition rule". All attempts to carry out this reaction under ionic conditions in the presence of additives inhibiting the free-radical reaction failed. Free-radical addition occurs also in the reaction of ethoxyacetylene with propane-1-thiol, thiophenol, and thiocresol.

Disubstituted acetylenes react similarly with mercaptans. In all cases the RS group adds at the β-carbon atom of the ether or sulphide [75]:

$$R-C\equiv C-OR(SR)+RSH \longrightarrow R-C(SR)=CH-OR(SR).$$

However, the addition of mercaptans to disubstituted acetylenes is slow and requires prolonged boiling and the

presence of free-radical initiators. The following reactions belong to this group: the reaction of ethoxypropyne with ethanethiol:

$$C_2H_5O-C\equiv C-CH_3+C_2H_5SH \longrightarrow C_2H_5O-CH=\underset{\displaystyle SC_2H_5}{C}-CH_3,$$

the reaction of ethoxy- and ethylthio-ethynylmethanols with ethanethiol[29]:

$$RR'C(OH)-C\equiv C-R''+C_2H_5SH \longrightarrow RR'C(OH)-\underset{\displaystyle SC_2H_5}{C}=CH-R'',$$

where R'' = OC_2H_5 or SC_2H_5, and the reaction of the ethylthiopropiolate ester with ethanethiol[80]:

$$ROOC-C\equiv C-SC_2H_5 \xrightarrow{C_2H_5S^{\cdot}} \left[ROOC-\underset{\displaystyle SC_2H_5}{C}=\dot{C}-SC_2H_5\right] \xrightarrow{C_2H_5SH}$$

$$\longrightarrow ROOC-\underset{\displaystyle SC_2H_5}{C}=CH-SC_2H_5+[C_2H_5\dot{S}].$$

The slower rate of the reactions with substituted ethynyl ethers compared with the similar reactions of unsubstituted ethynyl ethers and sulphides[75] can be understood from an examination of the polarisation of their molecules. Bonnema and Arens[80] believe that the reactions of the substituted ethers are slower because of the reduction of electron density at the second carbon atom resulting from the withdrawal of electrons to the carbonyl group:

$$O=\overset{\displaystyle OC_2H_5}{\underset{\displaystyle O}{C}}-\overset{2}{C}\equiv\overset{1}{C}-SC_2H_5.$$

In unsubstituted ethynylsulphides the electron density is concentrated at the second carbon atom by virtue of the free electron pair of the sulphur atom, which favours the formation of a new bond:

$$H-C\equiv C-SC_2H_5.$$

In one of their latest studies, Arens and coworkers[70] were able to carry out the nucleophilic addition of sodium ethanethiolate to ethoxyacetylene. It is known[75] that the ethoxy-group exhibits its electron-donor properties in nucleophilic and electrophilic addition reactions. In reactions of ethoxyacetylene with primary and secondary amines, alcohols, water, etc. the nucleophilic group always adds at the β-carbon atom of the ethoxyacetylene.

Accordingly, Alkema and Arens[79] were able to add sodium ethanethiolate (a nucleophilic reagent) to ethoxyacetylene in liquid ammonia. They found that under these conditions the addition also results in the formation of a 1,1-disubstituted ethylene:

$$CH\equiv C-OC_2H_5 \xrightarrow{C_2H_5SNa} CH_2=\underset{\displaystyle SC_2H_5}{\overset{\displaystyle OC_2H_5}{C}},$$

i.e. the ethylthio-group adds at the β-carbon atom in conformity with other nucleophilic addition reactions. Here too the alkoxy-group of the ethynyl ether exhibits its characteristic electron-donor properties.

Alkema and Arens were able to prove convincingly the structure of their products by infrared spectroscopy, hydrolysis, and the addition of ethanethiol followed by treatment with potassium hydrogen sulphate:

$$CH_2=\underset{\displaystyle SC_2H_5}{\overset{\displaystyle OC_2H_5}{C}} \xrightarrow{C_2H_5SH} C_2H_5S-CH_2-CH(OC_2H_5)(SC_2H_5) \xrightarrow{KHSO_4} C_2H_5S-CH=CH-SC_2H_5.$$

These results invalidate Truce's conclusion[55,60] that nucleophilic addition of mercaptans to acetylenic compounds results in the formation of 1,2-substituted ethylenes. Arens' attempts[79] to isolate the ethylenes which Truce obtained in this reaction were unsuccessful.

It follows that free-radical addition of mercaptans to ethynyl ethers and sulphides yields β-substituted sulphides. Under ionic conditions the reaction is stereospecific, in accordance with the "*trans*-addition rule", resulting in the formation of *cis*-ethylenes. Under very mild conditions it is possible to carry out nucleophilic addition of a mercaptan to ethynyl ethers and obtain α-substituted sulphides.

IV. ADDITION OF ALCOHOLS AND MERCAPTANS TO DIACETYLENES

1. Addition of Alcohols to Diacetylene

The addition of alcohols to diacetylene was first described in a patent[81] dealing with the preparation of ethynylvinyl ethers by this reaction. Then Franke[51,52] and Herberts[82] prepared methyl ethynylvinyl ether and investigated some of its properties. These investigations were the starting point of the development of the chemistry of unsaturated ethers synthesised by addition of alcohols to diacetylenes.

A systematic and detailed investigation of this reaction has been carried out since 1956 in the Laboratory of Vinyl Compounds of the Institute of General Chemistry of the USSR Academy of Sciences[53,83]. Aliphatic, alicyclic, and aromatic alcohols and other compounds containing reactive hydrogen, mercaptans[83-92], amines[93-95], lactams[96], etc., have been used in the reaction.

The reaction of diacetylenes with alcohols takes place in the presence of alkaline catalysts even when diacetylene is merely passed into the alcohol at 60–110° (depending on the alcohol), resulting in the formation of ethynylvinyl ethers and 1,1-dialkoxybut-2-yne:

$$CH\equiv C-C\equiv CH+ROH \longrightarrow CH\equiv C-CH=CH-OR \xrightarrow{ROH} CH_3-C\equiv C-CH(OR)_2.$$

Shostakovskii *et al.*[53] established that the reaction takes place in stages and that the yields of the ethynylvinyl ether and the acetal depend on the initial ratio of the reactants, the nature of the alcohol, the amount of catalyst, and especially on the reaction temperature. Thus on heating to 100–110°, only one alcohol molecule adds and the ethynylvinyl ether is formed; when the mixture is heated to 130° and above, a second alcohol molecule adds to the ethynylvinyl ether and the acetal is formed.

Later[86,88], this reaction was extended to benzyl alcohol and phenol, the corresponding ethynylvinyl ethers being obtained. A patent application[81] describes the preparation of an ethynylvinyl ether from phenol and diacetylene, but repeated attempts[86] to repeat this synthesis were unsuccessful, and the method is therefore doubtful.

In considering the mechanism of addition to diacetylene, the molecule of the latter can be regarded either as a conjugated system of triple bonds or as a substituted acetylene molecule in which one ethynyl group behaves as an electron-acceptor substituent in relation to the other, under the conditions of this reaction. Nieuwland and Bohlmann regarded the vinylacetylene and diacetylene molecules in terms of the first concept, this being apparently valid for alcohol addition reactions.

Adopting Nieuwland's hypothesis [47] of the formation of an intermediate allene structure when methanol adds to vinylacetylene,

$$CH_2{=}CH{-}C{\equiv}CH \xrightarrow{CH_3OH} [CH_3O{-}CH_2{-}CH{=}C{=}CH_2] \longrightarrow CH_3O{-}CH_2{-}C{\equiv}C{-}CH_3,$$

Bohlmann [97,98] proposed the following mechanism for the reaction of diacetylene with methanol:

$$CH{\equiv}C{-}C{\equiv}CH \rightleftarrows [HC^{+}{=}C{=}C{=}CH^{-}] \xrightarrow{RO^-} [RO{-}CH{=}C{=}C{=}CH^{-}] \xrightarrow{H^+} RO{-}CH{=}CH{-}C{\equiv}CH.$$

The action of the alkoxide results in the formation of an intermediate polar compound with a cumulative system of double bonds to which the alkoxy-group undergoes addition. The resulting complex anion is converted into an ethynylvinyl ether molecule after addition of a proton and subsequent isomerisation.

Bohlmann [98] also found that the formation of an allene structure is facilitated by an increase in the number of triple bonds, which accelerates the addition of the alcohol. Comparison of the conditions under which alcohols react with acetylene and diacetylene is instructive in this connection. Vinylation of alcohols with acetylene requires heating to 140–160° and an elevated pressure [3], while the addition of the same alcohols to diacetylene takes place at 60–125° under normal pressure [53].

Bohlmann [97,98] explained the formation of the intermediate with a cumulative system of double bonds by the tendency of the π electrons of the triple bonds to interact with one another whereby the electrons are uniformly distributed throughout the system, which can be represented as follows [13]:

$$CH{\equiv}C{-}C{\equiv}CH \longleftrightarrow H{-}\overset{+}{C}{=}C{=}C{=}\overset{-}{C}{-}H \text{ etc.}$$

Physical investigations confirm this. Examination of the C–C, C=C, and C≡C bond lengths in diacetylene, vinylacetylene, and acetylene molecules shows that single C–C bonds included between double and triple bonds are somewhat shorter [13]:

$HC{\equiv}C{-}C{\equiv}CH$	$CH_2{=}C{-}C{\equiv}CH$	$HC{\equiv}CH$	$CH_3{-}CH_3$.
1.19; 1.36; 1.19	1.36; 1.42; 1.20	1.20	1.54

The shortening of these bond lengths shows that in the above molecules there is partial double bond character. However, the similarity to olefinic compounds is very superficial, because pure cumulative polyenes do not add alcohols under the same conditions. For example, aliphatic cumulative pentaenes do not react with alcohol [97]. It is also known that the triple bond is more reactive with respect to nucleophilic reagents (alcohol, water, amines) than is the double bond, whereas with respect to electrophilic reagents (halogens, per-acids, ozone) the opposite is true [13].

2. Addition of Alcohols to Substituted Diacetylenes

Substituents in diacetylene have a major effect on its reactivity and the mode of the reaction. Monosubstituted diacetylenes are more reactive in alcohol addition reactions than are disubstituted acetylenes. Herberts [99,100] showed that the addition of methanol to methyl- or ethyl-diacetylene takes place when the mixture is heated in the presence of NaOH:

$$R{-}C{\equiv}C{-}C{\equiv}CH + CH_3OH \longrightarrow R{-}C{\equiv}C{-}CH{=}CH{-}OCH_3.$$

Dimethyldiacetylene virtually does not react under conditions in which alcohols add on diacetylene itself. More severe conditions are required for this reaction than in the case of alkyldiacetylenes: the mixture must be heated in a bomb under pressure for 14 h at 120°:[97]

$$CH_3{-}C{\equiv}C{-}C{\equiv}C{-}CH_3 \xrightarrow{CH_3OH} CH_3{-}C(OCH_3){=}CH{-}C{\equiv}C{-}CH_3.$$

This finding confirms Bohlmann's mechanism. In his view the electron-donating methyl groups hinder the formation of an intermediate structure with accumulative systems of double bonds and thereby inhibit the addition of the alcohol. However, the effect of the substituents diminishes with increase in the number of triple bonds. Thus ethanol adds much more easily to dimethyltriacetylene than to dimethyldiacetylene and its addition to dimethyltetraacetylene takes place on simple refluxing of the mixture in a flask for 2 h: [97]

$$CH_3[C{\equiv}C]_4CH_3 \xrightarrow[CH_3OH]{Na} CH_3[C{\equiv}C]_2{-}CH{=}C(OCH_3){-}CH_3.$$

The existing data on the reactions of polyynes [98] indicate that the terminal atom with a partial positive charge is responsible for the ease of the nucleophilic reactions.

3. Addition of Mercaptans to Diacetylene

Up to 1958 [85] only the preparation of an ethynylvinyl sulphide as the sole product of the reaction of diacetylene with butanethiol and toluene-ω-thiol under the influence of alkali, described in patents [84], was known. The reaction of diacetylene with mercaptans takes place in stages,

$$CH{\equiv}C{-}C{\equiv}CH + RSH \longrightarrow CH{\equiv}C{-}CH{=}CH{-}SR \xrightarrow{RSH} RS{-}CH{=}CH{-}CH{=}CH{-}SR,$$

and results in the formation of ethynylvinyl sulphides and dialkylthio(arylthio)buta-1,3-dienes. The reaction begins on mixing the starting materials in the presence of alkali and a diluent at room temperature and is accompanied by a rise in temperature. When gaseous acetylene is passed into a mixture of the mercaptan and alcoholic alkali, the latter must be heated to 50–55°. With ethane- and isopropane-thiol the second method of synthesis is more convenient, since the reaction takes place more smoothly without a jump in temperature.

The optimum temperature for the formation of ethynylvinylethyl and ethynylvinyl isopropyl sulphides is 50–55° and for ethynylphenyl sulphide 35–40°. The addition of the first mercaptan molecule to diacetylene yields an ethynylvinyl sulphide and the addition of the second molecule a 1,4-dialkyl(aryl)thiobuta-1,3-diene. The reviewers have shown that both stages have their own optimum conditions, for the maximum yield of the final product, and that they can take place independently.

When it is desired to obtain the ethynylvinyl sulphide, solvents must be used to increase its yield and to suppress the second stage. Since the reaction of diacetylene with mercaptans takes place more readily than with alcohols, the latter may be used as diluents, their hydroxyl hydrogen not being involved in the reaction. Methanol is particularly suitable for this purpose [90], but dioxan has also been used [85]. The reaction of diacetylene with mercaptans takes place vigorously, with rise in temperature, only in the presence of alkali. Azodiisobutyronitrile or heating alone do not

initiate the reaction, the yield of the ethynylvinyl sulphide not exceeding 10% under these conditions. We must therefore conclude that the addition of the first mercaptan molecule to diacetylene takes place by an ionic mechanism.

The action of alkali results in the formation of alkyl- or aryl-sulphide ions which cause a shift of electrons in the diacetylene molecule thereby facilitating the nucleophilic addition of the ions to the carbon atom having the least electron density:

$$CH{\equiv}C{\longleftarrow}\overset{\oplus}{C}{\equiv}CH + R\bar{S} \longrightarrow CH{\equiv}C{-}\bar{C}{=}CH{-}SR \xrightarrow{RSH} CH{\equiv}C{-}CH{=}CH{-}SR + R\bar{S}.$$

The addition of mercaptans to diacetylene under ionic conditions is stereospecific. Like other ionic reactions involving the addition of nucleophilic reagents, it takes place according to the "*trans*-nucleophilic addition rule", *cis*-isomers being formed [89,92,95].

The addition of a second mercaptan molecule requires more severe conditions. The reaction is not accelerated by alkaline catalysts (in "catalytic" amounts), requires heating in the presence of free-radical initiators (benzoyl peroxide, azodiisobutyronitrile), and is inhibited by antioxidants [91] (hydroquinone, triethanolamine, SO_2), *i.e.* the addition takes place by a free-radical mechanism.

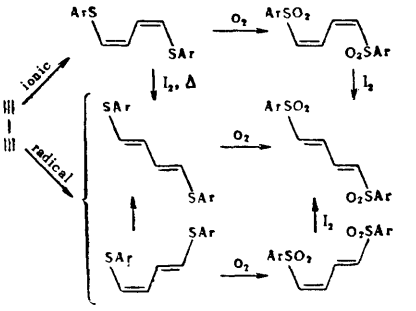
In considering the mechanism of the addition of mercaptans to diacetylene, the latter may be regarded as a monosubstituted acetylene. The available data show that the reaction is similar to that involving acetylenes with electron-acceptor substituents [43,44,55,68] in which the addition to the triple bond takes place across the 1,2-positions.

V. STEREOSPECIFIC SYNTHESES BASED ON DIACETYLENE AND MERCAPTANS

The problem of the stereochemistry of reactions involving the addition of mercaptans to diacetylene is still obscure. Studies of the conditions of the reaction between diacetylene and mercaptans and amines in the Laboratory of Vinyl Compounds [89,92,95] showed that the addition of the first mercaptan or amine molecule is an ionic reaction while the addition of the second molecule is a free-radical reaction. Thorough investigation of the products of this reaction showed that it is stereospecific, the stereospecificity depending on the mechanism.

It has been shown, for the addition of various mercaptans to diacetylene [89,92], that stereospecific synthesis of *cis*-*cis*-1,4-dialkylthio(arylthio)buta-1,3-dienes is possible under ionic conditions, while under free-radical or mixed conditions the addition results in a mixture of all three isomers, their proportions depending on the reaction temperature.

To establish the geometrical configuration of the stereoisomers obtained from butanethiol, the reaction mixture was oxidised and the resulting sulphones were separated by fractional crystallisation, whereby all three isomers were isolated [92]. Since in the case of thiophenol the resulting diphenylthiobuta-1,3-dienes are crystalline, the *cis*-*cis*-isomer was isolated directly from the reaction mixture and the remaining two isomers were isolated after oxidation of their mixtures to the corresponding sulphones [89]. The geometrical configurations of the stereoisomeric dialkylthio- and diarylthio-buta-1,3-dienes were assigned on the basis of their physical properties and isomeric transformations. The isomeric transformations of 1,4-diarylthiobuta-1,3-dienes are shown below:



The stereochemistry of the addition of alkylamines to diacetylene has also been investigated. Shostakovskii *et al.* [95] found that the addition of one diethylamine molecule to diacetylene under ionic conditions is stereospecific resulting in the formation of *cis*-diethylaminobutenyne whilst butylamine and diacetylene form a di-adduct with *cis*-*cis* configuration. Analysis of the available data shows that in an investigation of the stereochemistry of the addition of mercaptans and amines to diacetylene, the molecule of the latter must be regarded not as a system of conjugated multiple bonds but as a molecule of monosubstituted acetylene [90,92,95]. Consequently the reaction of diacetylene with mercaptans consists in the addition of two molecules of the latter to both triple bonds, as in the addition to mono- and di-substituted acetylenes, *i.e.* in accordance with the "*trans*-nucleophilic addition" rule; under ionic conditions the reaction is stereospecific with the formation of the corresponding *cis*-*cis*-isomers.

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CHEMISTRY OF 19-NORSTEROIDS

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1. INTRODUCTION

In the production of highly active steroidal compounds, it has been found that their hormonal activity can be increased (*i*) by introducing into the steroid molecule additional substituents, such as halogens, alkyl groups, and hydroxy-groups not normally present in the natural compounds, or (*ii*) by preparing compounds in which certain structural units present in natural steroids are missing. This class of compounds includes the 19-norsteroids, which do not have the methyl group at $C_{(10)}$ of the steroid skeleton.

Some 19-nor-compounds have a considerably higher activity than their 19-methyl analogues. For practical application, however, it is not so much the generally higher level of physiological activity of 19-norsteroids which is of importance, as their highly specific action in comparison with the natural steroids. Thus compounds have been prepared having high anabolic or anti-oestrogenic activity but practically no androgenic action; highly active gestagens, hypotensive and contraceptive agents, etc., have also been obtained. The high physiological activity of 19-norsteroids has led to their rapid introduction into medical practice and to an increased number of preparative studies in this field. It is difficult to find a section of organic chemistry which has developed so rapidly in the last 5–10 years as the study of modified steroid hormones, and of 19-norsteroids in particular. The index to *Chemical Abstracts* for 1950 contains only three references to 19-norsteroids, while for 1960 there are about 200. The only existing review of the chemistry of 19-norsteroids[1], which covers work appearing up to 1958, is thus considerably out of date.

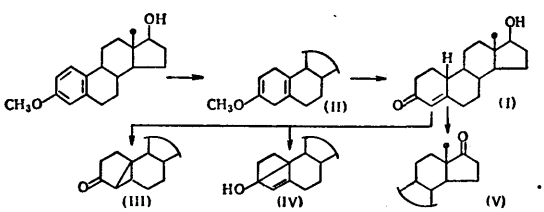
Because of limitations of space, we have used only reviews and the most important original papers in discussing the pharmacology and clinical use of 19-norsteroids, but the literature on their chemistry will be reviewed as fully as possible.

2. DERIVATIVES OF 19-NORANDROSTANE

(*a*) 19-Nortestosterone and Its Isomers

19-Nortestosterone (I) has been obtained by the Birch reduction of oestrone and oestradiol, alkaline treatment of 19-hydroxytestosterone, and various total syntheses.

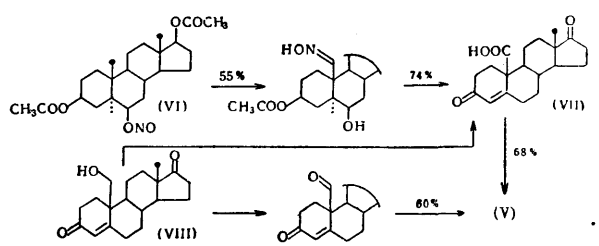
As starting materials Birch used ethers of oestradiol or oestrone. The reduction of glyceryl oestradiol ether by Birch's original procedure[2-4] gives (I) in yields of not more than 33%. Much better results are obtained from methyl oestradiol ether; hydrolysis of the resulting dihydro-derivative (II) with methanolic hydrogen chloride gives (I) in an overall yield of 80–90%.[5-8] The structure of (I) has been proved by its conversion to oestradiol by enzymatic dehydrogenation, and by its infrared and ultraviolet spectra[9-11]. The hydrogen atom at $C_{(10)}$ has the more stable, "natural" β-configuration, as has been shown by study of its optical rotatory dispersion[12,13] and nuclear magnetic resonance[14,15]. Oxidation of the 17-hydroxy--group of compound (III) with chromium(VI) oxide gives 19-norandrost-4-ene-3,17-dione (V).[6,16,17]. Photolysis of (I) in nitrogen produces a mixture of the 4,10- and 3,10--cyclosteroids (III) and (IV)†.[18]



19-Nortestosterone is obtained in practically quantitative yield by the alkaline treatment of 19-hydroxytestosterone, itself obtained by incubating testosterone with adrenal tissue or by partial synthesis from strophanthidin[19,20]. The 19-norandrostenedione (V) is also obtained by alkaline treatment of compounds oxidised at the 19-position. An important step in one preparation of (V)[21,22] is photolysis of 6β-hydroxy-3,17-diacetoxyandrostane nitrite (VI) (obtained from 3,17-diacetoxyandrost-5-ene) to the 19-aldoxime, which is dehydrated with phosphorus oxychloride in pyridine to give the corresponding nitrile; this is saponified and oxidised to produce the diketo-acid (VII), which is decarboxylated to the 19-norandrostenedione (V).

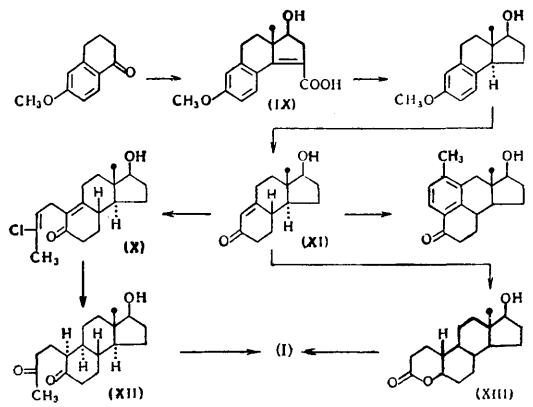
The compound (V) has also been prepared from the 6,19-oxide produced by oxidation with lead tetraacetate of the corresponding 5α-bromo-6β-hydroxy-compound[23].

Another method[24,25] starts from 19-hydroxyandrost-4--ene-3,17-dione (VIII), obtained by fermentation of the corresponding 19-deoxy-compound with *Corticium sasakii*. Oxidation of (VIII) with chromium (VI) oxide gives the diketo--acid (VII), which is converted to (V) as before. Mild oxidation gives the 19-aldehyde, which on heating with methanolic sodium hydroxide gives (V):



Various methods for the total synthesis of (I) from 1,2,3,4-tetrahydro-6-methoxy-1-oxonaphthalene have been described. In one of these[26,27] six steps yield the acid (IX), the laevorotatory isomer of which corresponds to the natural series. Decarboxylation of (IX) followed by selective hydrogenation gives a tricyclic compound containing the *B*, *C*, and *D* rings, which is reduced by Birch's method to the unsaturated ketone (XI). The usual method for attaching ring *A*, alkaline condensation with methyl vinyl ketone, gave only a product of cyclopentanophenalene structure when applied to (XI). Condensation with 1,3-dichlorobut-2-ene in the presence of sodium t-pentoxide gave compound (X), which on acid hydrolysis followed by catalytic hydrogenation yielded the diketone (XII); cyclisation of this with a mixture of hydrochloric and acetic acids was accompanied by epimerisation at $C_{(10)}$ and gave (I), identical in all respects with the natural compound.

Another method for preparing (I) starts from the racemic ketone (XI);[28] this is condensed with methyl acrylate in the presence of potassium t-butoxide to give an acid, which on catalytic hydrogenation and treatment with acetic anhydride gives the lactone (XIII), and this on reaction with methylmagnesium iodide followed by acidic cyclisation gives racemic (I):

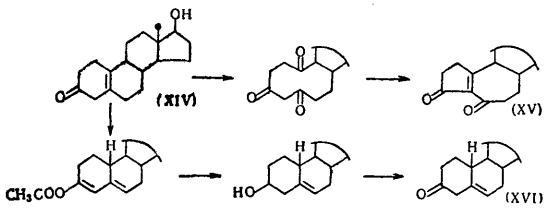


19-Nortestosterone (Nandrolone) has an anabolic activity equal to that of testosterone propionate, but its androgenic activity is only 6% of that of the latter; thus the ratio of anabolic to androgenic activity, which determines the clinical value of an anabolic agent, is 17 in 19-nortestosterone (taking that of testosterone propionate as unity). The product (I) also has strong anti-oestrogenic activity, weak gestagenic and anti-aldosteronic activity, and practically no oestrogenic, hypotensive, corticoidal, or anti--inflammatory activity[29-33].

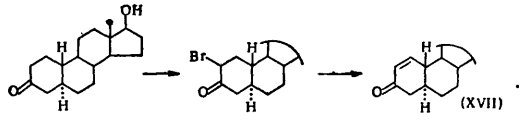
Since esterification of (I) produces compounds having a stronger and more lasting action on an organism, its esters have been widely investigated; they are usually prepared by treating (I) with the acid anhydride or chloride in the presence of pyridine or toluene-*p*-sulphonic acid. Esters of (I) have been described with the saturated aliphatic acids from formic to stearic[34-39], unsaturated aliphatic acids[35,37], and benzoic[40], hexahydrobenzoic[41,42], phenylacetic[35], and 3-phenyl- and 3-cyclopentyl-propionic acids[35,36]. The polyesters of (I) with succinic, glutaric, and phthalic acids are soluble in water, which is of importance for their practical application[35,43]. Esters have also been obtained with various amino-acids[44-46]. Of the esters of (I), only the 3-phenylpropionate (Durabolin) has found practical application as an anabolic agent, although good results in clinical trials have been shown also by the decanoate and the 3-cyclopentylpropionate[30-32].

† Here and subsequently, angular methyl groups will be represented by dots.

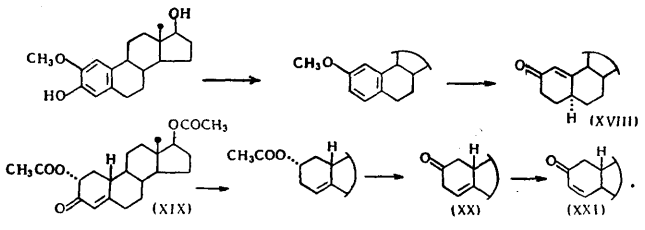
Isomers of (I) have been prepared for investigation of their physiological activity. Treatment with weak acids (oxalic or acetic), or ion-exchange resins of the Amberlite type, of the direct Birch reduction product of (II) gives an isomer of 19-nortestosterone having the double bond in the 5(10)-position (XIV).[6,47] This isomer has lower anabolic, androgenic, and gestagenic but higher oestrogenic activity than (I), and no anti-oestrogenic activity[31,48]. Ozonolysis of the acetate of (XIV) produces a triketone which on cyclisation in the presence of acetic acid gives compound (XV), which contains the so-called "abeosteroid" (*A*-nor-*B*-homosteroid) system[49]. The isomer of (I) with the double bond in the 5(6)-position (XVI) was obtained by sodium hydroborate reduction of the enol acetate of (I), with careful oxidation of the resulting 3,17-diol with chromium(VI) oxide. The physiological activity of this isomer is very like that of (I), apparently because of its ready isomerisation to the 4-en-3-one *in vivo*[50].



Compound (XVII), the isomer of (I) with the double bond in the 1(2)-position, was obtained from 4,5α-dihydro-19-nortestosterone by bromination followed by dehydrobromination, or by dehydrogenation by enzymes of *Pseudomonas testosteroni*. The 5β-epimer of (XVII) was prepared similarly[51-53]:



The isomer of (I) with the keto-group in the 2-position (XVIII) was obtained by reduction of 2-methoxyoestradiol, by way of the diethyl phosphate, to the 2-methoxy-compound, with subsequent Birch reduction; this isomer has very weak androgenic and anabolic activity[54,55]. Reduction of the keto-group of 2α-acetoxy-19-nortestosterone (XIX) by way of the corresponding ethylene thioketal gave an acetate which was hydrolysed and oxidised to the 4-en-2-one (XX); in acid medium this is converted into the 3-ene (XXI):[56,57]

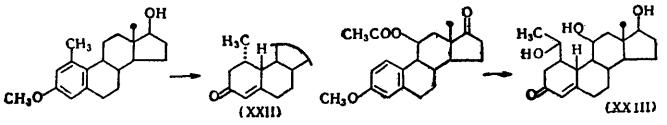


Reduction of 17-iso-oestradiol methyl ether with lithium in liquid ammonia has given the isomer of (I) with the 17-hydroxy-group in the α-configuration; this has neither androgenic nor anabolic activity[58].

Changing the position of the double bond or the keto-group or the configuration of the hydroxy-group in the molecule of (I) is thus seen to lead to a reduction in physiological activity.

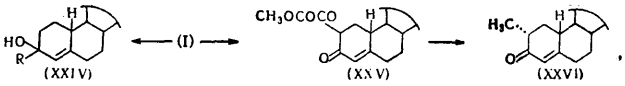
(*b*) Alkyl Derivatives of 19-Nortestosterone

The simplest *1-alkyl derivative* of (I) with a 1α-methyl group (XXII) has been prepared by Birch reduction of methyl 1-methyloestrone ether; the 1α,10β-configuration of (XXII) is based on its optical rotatory dispersion. 1α-Methyl-19-nortestosterone and its derivatives are not noticeably different in gestagenic and androgenic activity from their 1-demethyl analogues[59-61]. In the Birch reduction of 11β-acetoxyoestrone methyl ether the acetyl group migrates from the oxygen atom in the 11-position to the carbon at position 1 by a Claisen rearrangement type of mechanism, with the formation of compound (XXIII), which has anabolic, androgenic, and anti-oestrogenic activity[62,63].



2-Alkylation of (I) and its derivatives has been achieved by alkylation of the oxalyl derivative (XXV); the resulting 2α-methyl-19-nortestosterone (XXVI) has also been prepared by total synthesis by the method described above (Section 2*a*).[52,64,65]

3-Alkyl derivatives of (I) are obtained by reaction with chloroform and methyl- or butyl-magnesium bromide (XXIV):[6,67]

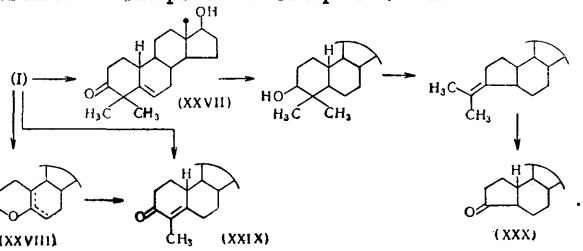


where R = CCl_3, CH_3, or C_4H_9.

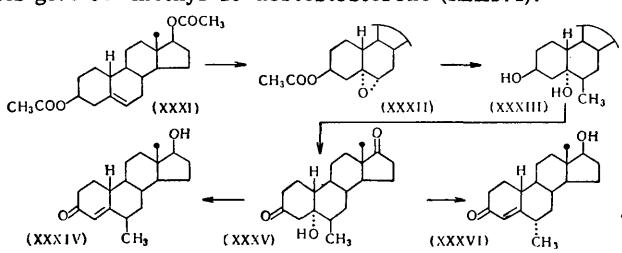
A *4-methyl group* is introduced into 19-nortestosterone by treatment of the lactone (XXVIII) — obtained from (I) by ozonolysis and lactonisation with acetic anhydride — with ethylmagnesium bromide, followed by alkaline cyclisation to 4-methyl-19-nortestosterone (XXIX).[68]

Reaction of the lactone (XXVIII) with ^{14}C-labelled methylmagnesium iodide followed by cyclisation gave 19-nor[4-^{14}C]testosterone, used as starting material for the production of oestrogens labelled in the 4-position[69-71]. Compound (XXIX), together with the 4,4-dimethyl derivative (XXVII), has been obtained also by alkylating (I) with methyl iodide in the presence of potassium t-butoxide[65,68,72]. The reduction product of the ketone (XXVII) treated with phosphorus pentachloride gives the isopropylidene derivative, which on ozonolysis produces *A*,19-dinortestosterone (XXX).[73,74]

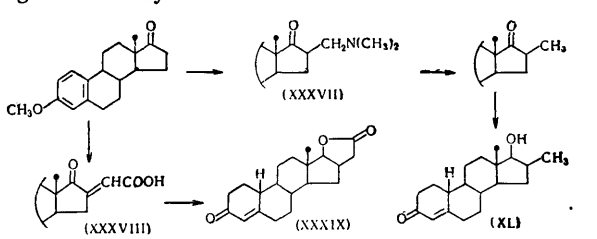
4-Alkyl-19-norandrostanes have been prepared also by catalytic hydrogenation of 1-hydroxy-4-methyloestra--1,3,5(10)-trien-17-one,[75] dehydration of 9α-hydroxyandrost-4-ene-3,17-dione,[76] and treatment of oestrone with allyl bromide in the presence of aqueous alkali[77].



5β-Methyl derivatives of (I) have been prepared by the Westphalen rearrangement and photolysis of 1-dehydrotestosterone acetate[78-80]. *6-Methyl homologues* of (I) have been obtained from the enol acetate of (I), the sodium tetrahydroborate reduction of which produces the dihydro derivative (XXXI), which is oxidised by monoperphthalic acid to the 5α,6α-oxide (XXXII); reaction of this with methylmagnesium iodide, and followed by oxidation of the resulting triol (XXXIII) with chromium(VI) oxide, gives the compound (XXXV), which is the main starting material for further preparations. Dehydration with thionyl chloride in pyridine, reduction of both keto-groups in the resulting ketone with lithium tetrahydroaluminate, and selective oxidation of the 3-hydroxy-group with manganese dioxide produce 6β-methyl-19-nortestosterone (XXXIV). Dehydration of compound (XXXV) with sodium hydroxide leads to a change of configuration, giving a diketone containing a 6α-methyl group; with the keto-group in the 3-position protected by formation of the ethyl enolate sodium tetrahydroborate reduction of the 17-keto-group and acid hydrolysis give 6α-methyl-19-nortestosterone (XXXVI):[81]



16β-Alkyl derivatives of (I) have been prepared from methyl oestrone ether, which by the Mannich reaction gives the amine (XXXVII), converted in two stages into methyl 16β-methyloestrone ether. Reduction of the 17-keto-group with sodium tetrahydroborate and of ring *A* by the Birch method gives 16β-methyl-19-nortestosterone (XL), which has high anabolic and antigonadotropic activity[82]. Condensation of methyl oestrone ether with glyoxylic acid produces the acid (XXXVIII); successive reduction with sodium tetrahydroborate, hydrogen over a platinum catalyst, and lithium in liquid ammonia has given the lactone of 16β-carboxymethyl-19-nortestosterone (XXXIX), which has antiandrogenic activity[83]:



17α-Alkyl derivatives of 19-nortestosterone (XLIII) are usually prepared by reaction of the appropriate Grignard reagent with 17-ketones of the 19-norandrostane series. Various methods have been worked out for preventing the 3-keto-group from being involved in the reaction, by varying the order in which reduction and alkylation are carried out and the methods of protecting the 3-keto-group:

A. Reaction of methyl oestrone ether with the Grignard reagent followed by Birch reduction of the 17α-alkyl derivative (XLI) to the compound (XLIII).[7,84-86]

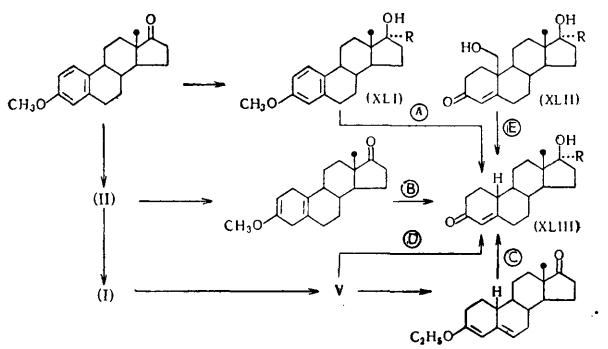
B. Oxidation with chromium(VI) oxide, or by the Oppenauer method, of the Birch reduction product of (II), reaction of the product with the Grignard reagent[87,88] or acetylene[89,90], and hydrolysis to a compound of the type (XLIII).

C. Oxidation of (I) with chromium(VI) oxide to the dione (V), protection of the 3-keto-group of (V) as the ethyl enolate, the pyrrolidine derivative, or the ethylene ketal[85,91-93], and reaction with the Grignard reagent or acetylene.

D. A specific method for 17α-ethynyl derivatives is the direct reaction of (V) with acetylene in the presence of alkaline reagents; this reaction proceeds only at the 17-keto-group[94].

Variants of these methods include reduction of unsaturated to saturated 17α-substituents either during the Birch reduction (method A) or by catalytic hydrogenation (methods B–D)[84,95-97].

E. A completely different method comprises perfusion of 17α-alkyltestosterones with adrenal tissue to obtain the 19-hydroxy-compounds (XLII), which after treatment with sodium hydroxide in aqueous methanol give 17α-alkyl-19--nortestosterones (XLIII).[98]

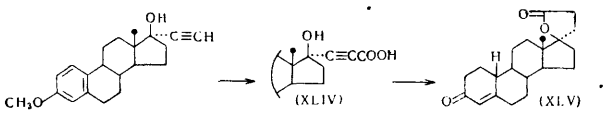


There exists a very large volume of literature on the physiological activity of 17α-alkyl-19-nortestosterones, including reviews[30-32,99,100]. The *anabolic activity* is at a maximum with the lower alkyl groups (CH_3, C_2H_5), when the ratio of anabolic to androgenic activity is 17 (testosterone propionate = 1). With lengthening of the alkyl chain, and the introduction of unsaturated substituents therein, both the anabolic and the androgenic activity are much decreased. 17α-Alkyl-19-nortestosterones are exceptionally active gestagens; as compared with progesterone they are 5–10 times as active when administered subcutaneously and more active by a factor of several powers of ten when administered orally. The gestagenic activity is greater with unsaturated substituents (vinyl, ethynyl, allyl, methallyl) and with substituents of the type –C≡CX, where X is alkyl or halogen.

Derivatives of (I) with 17α-alkyl substituents have practically no *oestrogenic* activity, but their 5(10)-ene isomers have 2–6% of the oestrogenic activity of oestrone. However, the 17α-alkyl-19-nortestosterones are powerful *anti-oestrogens*; thus in this respect the 17α-ethyl compound is 70 times as active as testosterone propionate and 12 times as active as progesterone [101,102]. Most compounds of this type inhibit ovulation and so are used as contraceptives [103–105]. The 17α-alkyl homologues of (I) are weak inhibitors of the growth of certain malignant tumours [106–108]. The 17α-alkyl-4-ene compounds also have a comparatively weak hypotensive action, which is completely absent in the 5(10)-ene isomers; neither series exhibits anti-inflammatory activity [109].

Four 17α-alkyl-19-nortestosterones are used medicinally and are prepared on an industrial scale: 17α-methyl--19-nortestosterone (Methyloestrenolone, Neosteron, Normethandrolone, Orgasteron) and 17α-ethyl-19-nortestosterone (Nilevar, Norethandrolone) mainly as anabolic agents, 17α-ethynyl-19-nortestosterone (Norlutin, Norethindrone, Norethisterone) as an oral progestative agent, and 17α-ethynyl-17β-hydroxyoestr-5(10)-en-3-one (Enovid, Norethynodrel, Ethynyloestrenolone) mainly as a contraceptive. The different types of activity of these compounds are compared in the Table; each has a fairly specific range of application.

If the steroid skeleton contains a 17-substituent of the type $[CH_2]_nCOOH$, cyclisation to form a spirolactone may occur. Thus the lactone of 17α-2′-carboxyethyl-19-nortestosterone (XLV) has been prepared by converting the Grignard derivative of 17α-ethynyloestradiol methyl ether to the acid (XLIV), catalytically hydrogenating this to the saturated acid, reducing its sodium salt with lithium in liquid ammonia, and hydrolysing the reduction product with hydrochloric acid [110,111]:



Compounds such as (XLV) are extremely active antagonists of mineralocorticoid hormones, especially (XLV) itself, known under the brand number SC-8109, which is four times as active as its 19-methyl analogue in blocking mineralocorticoids and has been used for treating various oedemas and primary hyperaldosteronism. The anticorticoidal activity is reduced if the double bond in the 4-position is hydrogenated or replaced by a 5(10)-double bond or if the lactone ring is expanded. The presence of an 11α--hydroxy- or 11-oxo-group greatly reduces the activity, while an 11β-hydroxy-group slightly increases it; it has also been reported that the introduction into SC-8109 of a 6-double bond and a 7-thioacetyl group increases the activity [111–113].

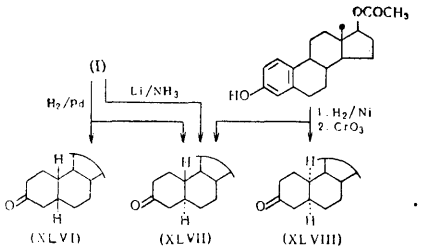
TABLE. Physiological activity of 17α-alkyl-19-nortestosterones.

Trade name	Type of activity						
	gestagenic	anabolic	androgenic	oestrogenic	anti-oestrogenic	inhibition of ovulation	hypotensive
Neosteron	++	++	+	0	++	+	0
Nilevar	++	++	+	0	++	+	+
Norlutin	++	+	+	0	+	+	0
Enovid	+	0	0	+	0	++	0

++ high activity
+ weak activity
0 practically no activity

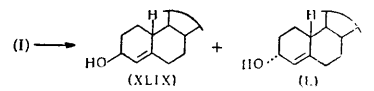
(c) Reduction Products of 19-Nortestosterone

Reduction of the double bond of (I) with lithium in liquid ammonia accompanied by decomposition of the reaction mixture by means of ammonium chloride gives the 5α,10β-dihydro-derivative (XLVII). [114] Catalytic reduction of (I) over ruthenium dioxide or palladium gives a mixture of the 5α,10β-isomer (XLVII) and the 5β,10β-isomer (XLVI). [114–117] A third series of isomers, with the 5α,10α-configuration (XLVIII), was obtained, together with an equal quantity of the 5α,10β-isomer (XLVII), by hydrogenating oestradiol 17-acetate over Raney nickel, followed by chromium(VI) oxide oxidation of the 3-hydroxy-group and hydrolysis of the 17-acetate residue [117]. Isomers having the 5β,10α-configuration would require a boat conformation for ring *B* and are apparently less stable; none have yet been prepared.



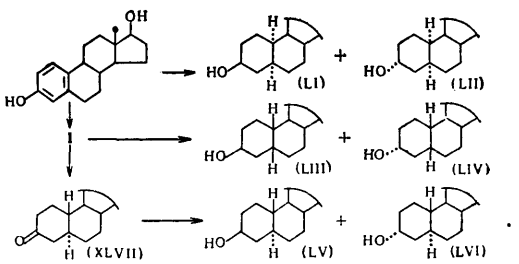
Hydrogenation of the 4-double bond of derivatives of (I) greatly reduces the anabolic, androgenic, and gestagenic activity, which also depend on the configuration at $C_{(5)}$ and $C_{(10)}$: the 5α,10β-compounds (XLVII) are the most active, and the 5β,10β-compounds (XLVI) the least; the 5α,10α--compounds (XLVIII) have a hormonal activity at all. The 5α,10β- and 5β,10β-dihydro-compounds also have strong anti-oestrogenic and hypotensive properties [101,118].

Reduction of the 3-keto-group of (I) with lithium tetrahydroaluminate or sodium tetrahydroborate gives a mixture of isomers containing the 3β-isomer (XLIX) and the 3α-isomer (L) in the ratio of about 2:1. [119,120] This reduction lowers the anabolic and androgenic activity but leaves the gestagenic activity apparently unaffected [30,31,50]:

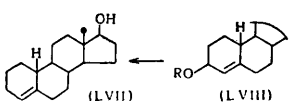


Complete reduction products of (I), the oestrane-3,17--diols, are found in human urine (5β,10β-series) [121–123], and are also products of the metabolism of (I) by homogenates of rat liver (5α,10β-series) [124]. The first preparations of this type of compound were achieved by exhaustive hydrogenation of oestrogen hormones over platinum oxide in alcohol containing hydrogen chloride [124–129] or over nickel–copper or nickel–chromium catalysts [130]. The products, as was shown later, were mixtures of diols of the 5β,10β-series with products of the hydrogenolysis of one or both hydroxy--groups.

All six possible isomers of oestrane-3,17β-diol of the 5α,10α-, 5β,10β-, and 5α,10β-series have now been prepared[114-117,131-133]. A mixture of isomers of the 5α,10α--series (LI) and (LII), with the 3β-hydroxy-isomer greatly predominating, was obtained by hydrogenating oestradiol over ruthenium dioxide; the isomers of the 5β,10β-series (LIII) and (LIV) were obtained as by-products. It is interesting that hydrogenation of oestradiol over Raney nickel gives approximately equal amounts of isomers of the 5α,10α- and 5α,10β-series; the direction of hydrogenation of oestrogens thus depends greatly on the catalyst used. Exhaustive hydrogenation of (I) over palladium on carbon gives a mixture of isomers (LIII) and (LIV) of the 5β,10β--series, with the former predominating; reduction of (I) with excess lithium in liquid ammonia leads exclusively to the 3β-hydroxy-isomer (LIII). Oxidation of the 3β-hydroxy--compounds (LI) and (LIII) with chromium(VI) oxide followed by reduction with sodium in propanol produces the corresponding 3α-isomers (LII) and (LIV). Finally, the mixture of isomers (LV) and (LVI) of the 5α,10β-series was obtained by hydrogenating the 4,5α-dihydro derivative (XLVII) over Raney nickel. Treatment of the toluene-*p*--sulphonate of the 3β-isomer (LV) with potassium acetate in dimethylformamide gives the 3α-isomer (LVI). While the isomers of the 5α,10α-series are inactive, the 5α,10β- and 5β,10β-compounds exhibit anabolic, androgenic, and hypotensive activity, but at a much lower level than the 4-en-3-one compounds.

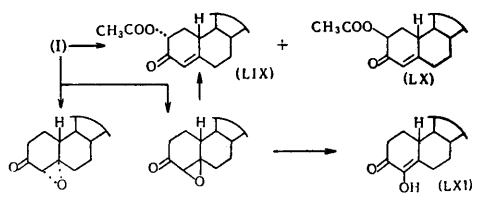


The simplest method for preparing *3-deoxy-compounds* of the 19-norandrostane series (LVII) is the Birch reduction of oestradiol in ethylamine or methylamine[134-136]; a more complex method consists in reduction of the methyl ethers or acetates (LVIII) to (LVII) with lithium in ethylamine[137-139]; (I) can also be converted into (LVII) by hydrogenolysis of the corresponding ethylene thioketal[56,140]. Finally, 3-deoxy-compounds with a double bond in the 2-position can be prepared by dehydration of the corresponding 3-hydroxy-compounds[133,141]. The 3-deoxy-compounds exhibit the same gestagenic activity as the 4-en-3--one compounds, and also anabolic and androgenic activity, but the level of this is unknown[140,141]:

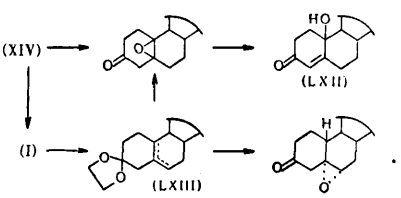


(*d*) Oxidation Products of 19-Nortestosterone

A preparative method for 2-hydroxy-compounds is lead tetraacetate oxidation of (I) acetate, to give a mixture of epimeric 2-acetoxy-derivatives in which the α-isomer (LIX) is present to a much greater extent than the β-isomer (LX).[142,143] Another method starts from the 4β,5β-oxide of (I), which undergoes rearrangement, under the influence of potassium acetate in acetic acid, to 2α-acetoxy-19-nortestosterone (LIX).[144-146] Opening of the 4β,5β-oxide ring with a mixture of sulphuric and acetic acids gives 4-hydroxy-19-nortestosterone (LXI), which has not gestagenic activity[147,148]; this compound is also obtained by the aerial oxidation of 4,5α-dihydro-19-nortestosterone (XLVIII) dissolved in t-butanol containing potassium t-butoxide, while under analogous conditions the 4,5β-dihydro-derivative (XLIX) gives the corresponding 1-en-2-ol:[149-151]

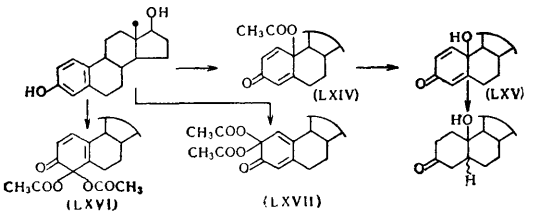


An oxygen substituent is introduced into the 6-position by fermentation of (I) with *Rhizopus nigricans* and by the perbenzoic acid oxidation of the enol acetate of (I).[152,153] Derivatives of (I) with a 10β-hydroxy-group have been obtained by several methods, for example from the 5β,10β-oxide obtained by the monoperphthalic acid oxidation of the 5(10)-ene (XIV).[154] This oxide is also prepared from 19-nortestosterone ethylene ketal (LXIII), which is a mixture of the 5(6)-ene and the 5(10)-ene in the ratio 2 : 1, as has been shown by epoxidation to the 5α,6α- and 5β,10β--oxides[155]. Opening the 5β,10β-oxide ring by boiling with methanolic potassium hydroxide produces 10β-hydroxy-19--nortestosterone (LVII).[154] The compound (LXII) has been prepared also by direct oxidation of the 5(10)-ene (XIV) with perbenzoic acid or osmium tetroxide, and, as a by--product, by fermenting (I) with *Rhizopus nigricans*[52]. The compound (LXII) possesses gestagenic and anabolic activity at a level several times lower than that of (I):[31,154]



The 10-hydroxy-derivatives of (I) with a double bond in the 1(2)-position are obtained by the lead tetraacetate oxidation of oestrone and oestradiol[156-164]; a mixture of the three products comprising the quinol acetate (LXIV) and the *gem*-diacetates (LXVI) and (LXVII) was obtained in a total yield of about 25%. The compound (LXIV) has oestrogenic activity and is apparently an antagonist of gestagenic agents; the compound (LXVI) exhibits oestrogenic properties which do not produce the usual anti-hormonal reactions. Reduction of the acetate (LXIV) with zinc dust in acetic acid or by catalytic hydrogenation gives oestrone; its hydrolysis under mild conditions produces 10β,17β-dihydroxy-oestra-1,4-dien-3-one (LXV), which is more stable than

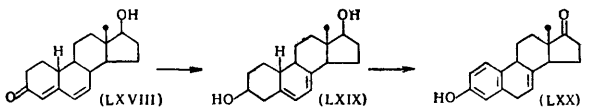
the acetate (LXIV); thus hydrogenation over palladium proceeds with retention of the 10-hydroxy-group, giving the 5ξ-tetrahydro-derivative:



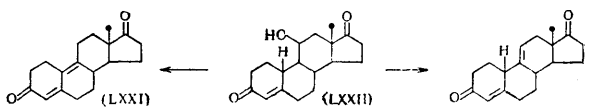
The 11α-hydroxy-derivative of (I) is obtained when the latter is fermented with *Rhizopus nigricans* [113], and also by the Birch reduction of oestrogens containing a 11α-hydroxy--group introduced by the same method [165]. 11β-Hydroxy--compounds are obtained by direct 11β-hydroxylation of (I) by perfusion with blood plasma or adrenal tissue [113], reduction of 11β-hydroxyoestrogens [69,165], and removal of the side-chain from 19-norcorticosteroids [166,167]. The 11α- and 11β-hydroxy-derivatives of (I) possess anabolic and androgenic activity [31,62]. Fermentation of (I) with *Mucor griseocyanus* and with *Penicillium urticae* give the 14α- and 15ξ-hydroxy-derivatives respectively [168,169]. Birch reduction of the methyl ether of oestriol gives 16α-hydroxy--19-nortestosterone, which has neither anabolic nor androgenic activity [170,171].

(*e*) Dehydrogenation Products of 19-Nortestosterone

The enzymatic introduction of a 1-double bond into ring *A* of 19-nortestosterone by means of *Pseudomonas testosteroni* [53,172,173], *Septomyxa affinis* [174,175], *Bacillus sphaericus* [176], *Corynebacterium simplex* [71,171], or *Protaminobacter alboflavum* [178] is accompanied by immediate aromatisation of the initially formed 1,4-diene into oestradiol. The 6-dehydro-derivative (LXVIII), which has a strong gestagenic action, is obtained from (I) by bromination followed by dehydrobromination, by dehydrogenation with benzoquinone or chloranil, or by oxidation with manganese dioxide [179,180]. Equilin was first prepared from compound (LXVIII) by reduction of its enol acetate with sodium tetrahydroborate to (LXIX), which by the Oppenauer oxidation gave the diketone, the 7(8)-double bond being preserved; enzymatic dehydrogenation of this with *Corynebacterium simplex* produced equilin (LXX): [179,181]

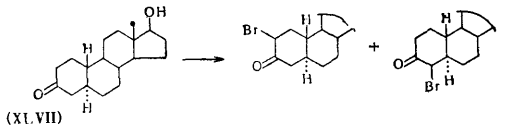


Direct bromination of (I) or its 5(10)-ene isomer in pyridine gives a high yield of the 9,10-dehydro-derivative (LXXI), also obtained by dehydration of the 11β-hydroxy--compound (LXXII) under severe conditions. Dehydration of (LXXII) under mild conditions gives the 9,11-dehydro--derivative. All these compounds possess considerable anabolic, gestagenic, and anti-oestrogenic activity [48,167,182,183].

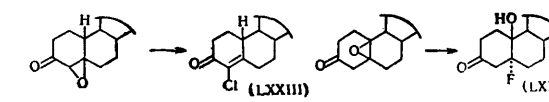


(*f*) Halogen Derivatives of 19-Nortestosterone

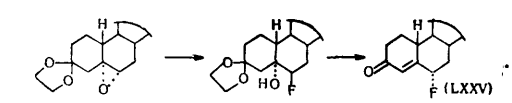
The anabolically active 2-halogeno-derivatives of (I) are prepared by direct halogenation of the 4,5α-dihydro-derivative (XLVII). The absence of the screening effect of a 19-methyl group considerably alters the stereochemical direction of bromination: while 4,5α-dihydrotestosterone gives only the equatorial 2α-bromo-ketone, bromination of the 19-nor-analogue (XLVII) gives a mixture of the axial 2β- and 4β-bromo-ketones in the ratio 1.5–2 : 1: [51,52]



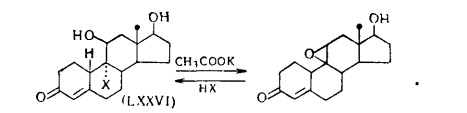
The main method for preparing a 4-halogeno-derivative of (I) is treatment of the 4β,5β-oxide with the corresponding aqueous hydrogen halide [116,144,145,184]. 4-Chloro-19-nortestosterone (LXXIII) has been obtained by direct chlorination of (I) [185] and by treating it with isocyanuryl chloride [186] or t-butyl hypochlorite [187]. Reaction of the pyrrolidine derivative of (I) with perchloryl fluoride has been suggested [188] for preparation of the 4-fluoro-derivative. 4-Chloro-19-nortestosterone has a ratio of anabolic to androgenic activity of 28 (activity of testosterone propionate = 1); it also has marked anti-oestrogenic action and weak gestagenic activity [144,148]. The opening, with boron trifluoride, of the ring of the 5β,10β-oxide obtained from the 5(10)-ene isomer of (I) gives the 5α-fluoro-10β--hydroxy-derivative (LXXIV), which has one-quarter of the gestagenic activity of Norlutin [154,155].



Halogen is introduced into the 6-position of (I) by ring--opening of the 5α,6α-oxide with hydrogen fluoride or boron trifluoride; the resulting fluorohydrin is dehydrated with anhydrous hydrogen chloride, with accompanying inversion at $C_{(6)}$, to give 6α-fluoro-19-nortestosterone (LXXV): [155]

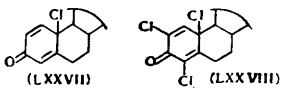


Reaction of the 9,11-dehydro-derivative of (I) with hypobromous acid produces the bromohydrin (LXXVI; X = Br), which with potassium acetate gives the 9β,11β-oxide; ring--opening of this with hydrogen fluoride, hydrogen chloride, or hydrogen iodide gives the corresponding 9α-halogeno--11β-hydroxy-derivatives of (I), which exhibit anabolic activity [189,190]:



Reaction of oestradiol with isocyanuryl chloride or *N*-chlorosuccinimide gives 10β-chloro-Δ¹-19-nortestosterone (LXXVII) in 25% yield; with the former, the

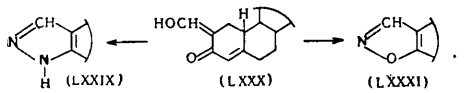
2,4,10β-trichloro-derivative (LXXVIII) is obtained as a by-product, and with the latter, a dichloro-derivative of undetermined structure. With perchloryl fluoride, oestradiol forms 10β-fluoro-Δ^1-19-nortestosterone, which is slightly more stable than its 10β-chloro-analogue (LXXVII); thus it can be hydrogenated to the saturated ketone without loss of the 10β-fluoro-atom. Compounds (LXXVII) and (LXVIII) have oestrogenic and anti-androgenic activity[191,192].



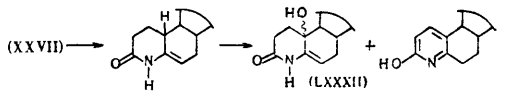
(*g*) Heterocyclic Derivatives of 19-Nortestosterone

Structurally the heterocyclic derivatives of (I) fall into two groups — those in which the heterocyclic system is fused to ring *A*, and those in which a carbon atom of the skeleton is replaced by a hetero-atom.

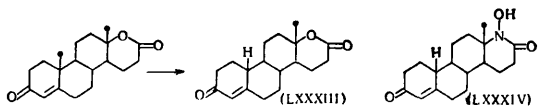
Derivatives of the first group are prepared by treating the 2-hydroxymethylene derivative (LXXX) or its 4,5α-dihydro-analogue with hydrazine hydrate to produce pyrazo--derivatives (LXXIX), or with hydroxylamine to produce isoxazolo-derivatives (LXXXI); the former have high anabolic and oestrogenic activity, and the latter high gestagenic activity[193-196]:



The lactone (XXVIII), obtained by ozonising the acetate of (I), is converted into the 4-aza-derivative by passing a stream of ammonia through a benzene solution. This compound is oxidised by selenium dioxide to (LXXXII), together with small amounts of 4-aza-oestradiol mono- and di-acetates[197,198]:

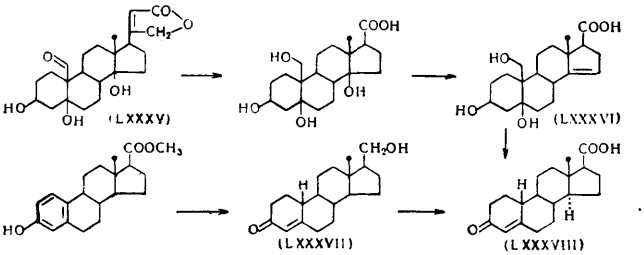


The analogue of (I) with an oxygen atom in ring *D* (LXXXIII) has been obtained from an oxidation product of testosterone, the so-called testololactone; perfusion of adrenal tissue with this gives the 19-hydroxy-compound, which loses formaldehyde under the conditions of the Oppenauer reaction to form the compound (LXXXIII).[199] Photolysis of the nitrite of (I) has given the compound (LXXXIV) with a nitrogen atom in ring *D*.[200]

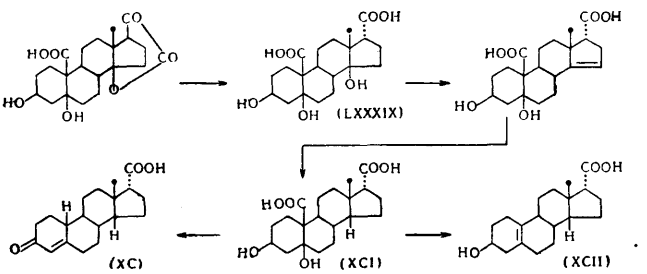


3. 19-NORETIANIC ACIDS

The 3-oxo-19-norandrost-4-ene-17β-carboxylic acid (LXXXVIII) has been prepared from strophanthidin (LXXXV): reduction of the latter with aluminium amalgam followed by oxidation with neutral potassium permanganate produced the tetrahydroxy-acid with a normal configuration of the side-chain; removal of the 14-hydroxy-group by heating with ethanolic hydrogen chloride gave the unsaturated acid (LXXXVI), which, like other 17β-substituted steroids, is catalytically hydrogenated to the 14α-dihydro-compound; successive treatment of this with *N*-bromoacetamide and Girard T reagent gives the acid (LXXXVIII).[201-203] In another method, methyl 3-hydroxy-19-norandrosta--1,3,5(10)-triene-17β-carboxylate is subjected to Birch reduction to obtain the compound (LXXXVII), which is oxidised by chromium(VI) oxide to the acid (LXXXVIII):[204]



An isomer of the acid (LXXXVIII), 3-oxo-19-nor-14β--androst-4-ene-17α-carboxylic acid (XC), has been obtained from strophanthidin (LXXXV) by a modified method[205-212]. Oxidation of strophanthidin 3-acetate with alkaline potassium permanganate gives a 33% yield of the lactone of the keto-carboxylic acid; treatment of this with alkaline hydrogen peroxide results in opening of the lactone ring, inversion at $C_{(17)}$ to the α-isomer, which is more stable for the *cis-C/D* series, and further oxidation to the dicarboxylic acid (LXXXIX). Dehydration of this acid with hydrogen chloride gives the 14(15)-ene, which, like other 17α-steroids, is catalytically hydrogenated to the 14β-compound (XCI), and this when oxidised with *N*-bromoacetamide loses the 5-hydroxyl and the 19-carboxyl to form the acid (XC). Thermal dissociation of the diacetate of (XCI) followed by hydrolysis produces the hydroxy-acid (XCII). The isomeric etianic acids (LXXXVIII), (XC), and (XCII) have been used as starting materials for the production of the corresponding 19-norprogesterone isomers (see Section 4).



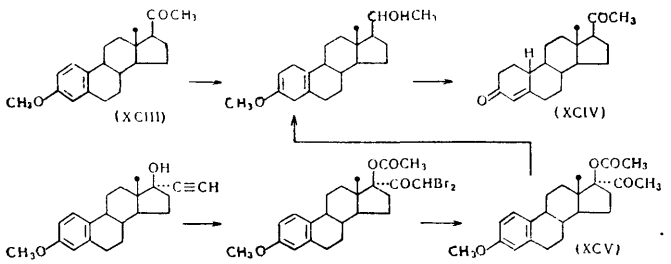
4. DERIVATIVES OF 19-NORPREGNANE

(*a*) 19-Norprogesterone

This compound has been obtained by total synthesis by a modified Woodward method[213], and by partial synthesis by four other methods. The starting material for the first of these was 5α-pregnane-3,20-dione; this was converted into the methoxy-ketone (XCIII), which by Birch reduction

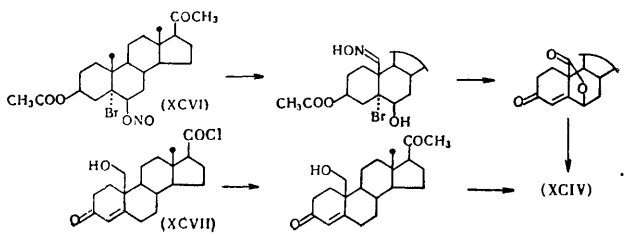
gave a compound with a 20ξ-hydroxy-group. Hydrolysis of the latter with hydrochloric acid and oxidation with chromium(VI) oxide gave 19-norprogesterone (XCIV) in a yield of 55% based on (XCIII).[214,215]

In another method, 17α-ethynyloestradiol methyl ether is converted with *N*-bromoacetamide by the Favorsky reaction into a dibromo-ketone. Debromination with zinc dust produces the 17α-acetyl derivative (XCV), which when reduced with lithium in liquid ammonia eliminates the 17-acetoxy-group and isomerises the other 17-substituent to produce the 20ξ-hydroxy-compound, which is then converted into (XCIV):[216]

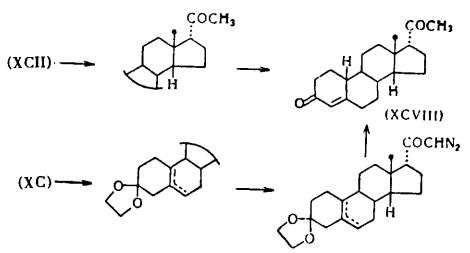


In a third method of preparing (XCIV), hydroxypregnenone is treated successivly with hypobromite and nitrosyl chloride to obtain the 5α-bromo-6-nitrite (XCVI), which on photolysis produces the 19-aldroxime; hydrolysis, oxidation, and dehydrobromination then gives the Δ⁴-3-oxo-lactone, which with zinc in acetic acid produces (XCIV).[22]

In the fourth method, the 19-hydroxyetienoyl chloride (XCVII) is converted by diazomethane into the corresponding diazo-ketone, which is reduced by hydrogen iodide to 19-hydroxyprogesterone. Treatment of this with aqueous sodium hydroxide gives (XCIV), identical with the product obtained by other methods[19,217-220]. 19-Norprogesterone has approximately eight times the gestagenic activity of progesterone and thirteen times its anti-oestrogenic activity[215,221,222]:



The isomer of (XCIV) with the 14β,17α-configuration (XCVIII) was the first 19-norpregnane to be synthesised; it was obtained in low yield from strophanthidin in 1944.[223] The synthesis was subsequently much improved, and is now carried out as follows[203-205]:

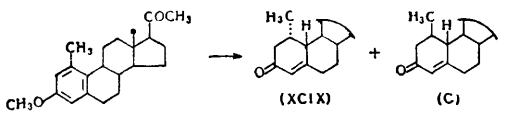


The etienic acid (XCII) treated with oxalyl chloride gives the acid chloride, which on reaction with dimethylcadmium followed by hydrolysis produces the corresponding keto-alcohol, and this is oxidised by the Oppenauer method to 19-nor-14β,17α-progesterone (XCVIII). The ketone (XCVIII) has also been prepared from the ethylene ketal of the acid (XC) by successive treatment with oxalyl chloride and diazomethane to give the diazo-ketone, which is reduced to compound (XCVIII) in a total yield of 25%. Compound (XCVIII) has about eight times the gestagenic activity of progesterone[224,225].

Even such considerable structural changes as removal of the 19-methyl group, *cis*-conjunction of rings *C* and *D*, and α-configuration of the side-chain, which is the inverse of the natural configuration, are thus seen to produce a considerable increase in hormonal activity over that found in the natural compound. In this respect it is interesting that the 15-methyl analogue of (XCVIII), 14β,17α-progesterone, has no gestagenic activity[226], demonstrating that there is no simple additive method for correlating physiological activity with structural changes in the steroid molecule.

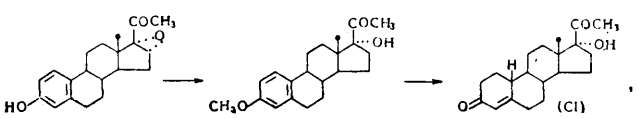
(*b*) Derivatives of 19-Norprogesterone

The compounds reviewed in this section are generally obtained analogously to the corresponding derivatives of (I). Thus reduction of 17β-acetyl-3-methoxy-1-methyloestra-1,3,5(10)-triene with lithium in liquid ammonia followed by chromium(VI) oxide oxidation of the resulting 20ξ-hydroxy-compound gives a mixture of the gestagenically active 1α-isomer (XCIX) and inactive 1β-isomer (C) of 1-methyl-19-norprogesterone[60,227]. 16α-Methyl-19-norprogesterone was prepared similarly[228].



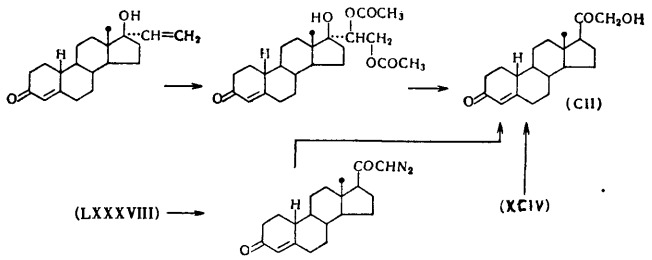
3-Deoxy-derivatives of 19-norprogesterone[137,139], Westphalen rearrangement products[80,229], and 9,10-dehydro-[182] and 4-chloro-19-norprogesterone[184] have been prepared analogously to the corresponding compounds of the 19-nor-androstane series. Fermentation of 19-norprogesterone with *Rhizopus nigricans* gives the 11α-hydroxy-derivative, and with *Curvularia linata* the 11β-hydroxy-derivative[230,231]. Fermentation with *Bacillus sphaericus* or *Corynebacterium simplex* gives the corresponding phenol[176,230,231]. Finally, the enzymes of *Helicostylum piriforme* and *Mucor griseocyanus* give the 14α-hydroxy-derivative[231] and those of *Penicillium urticae* a 15ξ-hydroxy-derivative[232].

17α-Hydroxy-19-norprogesterone (CI), which has high progestative activity, has been prepared from the 16α,17α-oxide; this is converted in three steps to the 17α-hydroxy-compound, which is reduced by the Birch method to (CI) in a total yield of up to 35%.[167] Fermentation of 17α-hydroxyprogesterone with *Corticium sasakii* or with adrenal homogenates and alkaline treatment of the resulting 19-hydroxy-compound also produces (CI).[25,233]

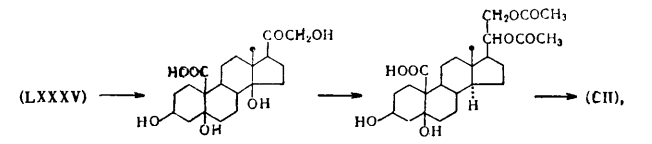


(*c*) 19-Nordeoxycorticosterone

The simplest method for obtaining this compound is 21-hydroxylation of 19-norprogesterone with enzymes of *Aspergillus niger*; the yield reaches 48%.[234] In another method, 17α-vinyl-19-nortestosterone is oxidised with osmium tetroxide and then acetylated to the 20,21-diacetoxy--derivative, which on boiling with zinc dust in toluene gives (CII).[204,235] In a third method, the acid (LXXXVIII), obtained from strophanthidin (see Section 3), is converted into the acid chloride, and this is treated with diazomethane to produce the diazo-ketone, which on heating with acetic acid gives (CII).[204,218]. Application of these reactions to the 14β,17α-isomer of (XC), which is also obtained from strophanthidin, gives the corresponding isomer of (CII), which is devoid of mineralocorticoid activity[205,223]:



Recently an original method for preparing 19-nordeoxycorticosterone (CII) directly from strophanthidin (LXXXV) has been proposed: ozonolysis of (LXXXV) gives the required side-chain directly, with simultaneous oxidation to the 10-carboxylic acid. Removal of the 14-hydroxy-group with hydrogen chloride yields the 14(15)-unsaturated compound, which when hydrogenated over a platinum catalyst forms the triacetate. Selective hydrolysis of this compound followed by chromium(VI) oxide oxidation with simultaneous decarboxylation gives the acetate of (CII).[236] 19-Nordeoxycorticosterone acetate, when tested for retention of sodium in adrenalectomised rats, was five times as active as its 19-methyl analogue[233,237].

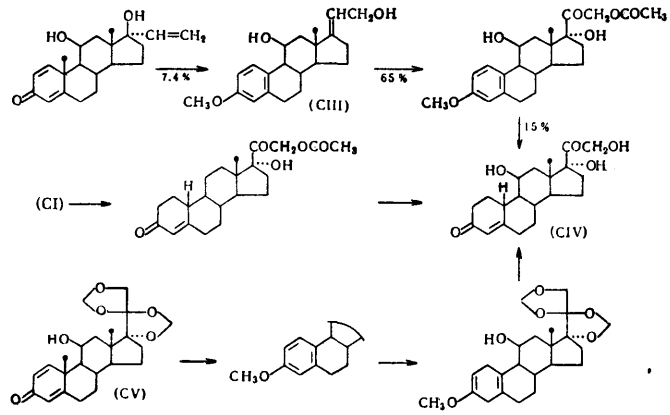


(*d*) 19-Norhydrocortisone

Three different methods have been proposed for the synthesis of 19-norhydrocortisone.

(i) 11β,17β-Dihydroxy-17α-vinylandrosta-1,4-dien-3-one is converted in five steps into the compound (CIII); successive oxidation of the side-chain with osmium tetroxide and *N*-methylmorpholine peroxide and acetylation of the product gave a compound having a dihydroxyacetone side-chain, the ethylene ketal of which is subjected to Birch reduction; acid hydrolysis of the product gives 19-norhydrocortisone (CIV). Oxidation of the 11β-hydroxy-group then yields 19-norcortisone[166].

(ii) 17α-Hydroxy-19-norprogesterone (CI) is treated with iodine in an alkali medium, and the resulting 21-iodo--derivative treated with potassium acetate to yield the 21-acetate. Introduction of the 11β-hydroxy-group by perfusion with adrenal homogenates gives 19-norhydrocortisone (CIV).[167,238]



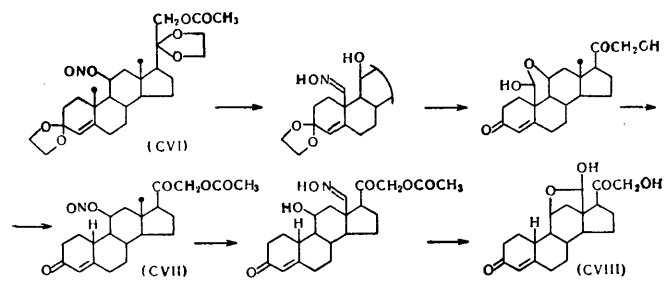
(iii) Pyrolysis of the bismethylenedioxy-derivative of prednisolone (CV) in mineral oil, followed by methylation, Birch reduction of the ether, and acid hydrolysis of the resulting dihydro-derivative gives 19-norhydrocortisone (CIV).[239]

19-Norhydrocortisone has one-tenth of the glucocorticoid activity and one-third of the anti-inflammatory activity of hydrocortisone, and one-quarter of the mineralocorticoid activity of deoxycorticosterone[166,167,240,241].

(*e*) 19-Noraldosterone

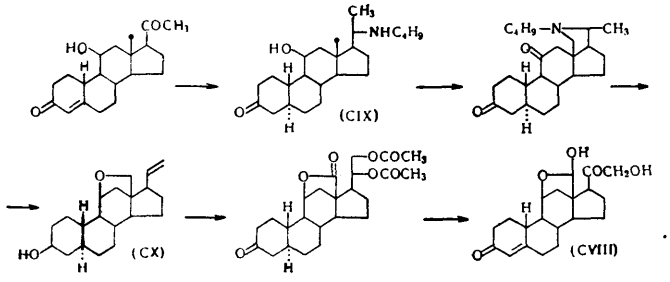
19-Noraldosterone (CVIII) has been prepared by two methods.

(i) The 11-nitrite 21-acetate of 3,20-bisethylenedioxy-pregn-4-ene-11β,21-diol (CVI) was photolysed to a mixture of 18- and 19-oximes; reaction of the latter with nitrous acid followed by hydrolysis gave the 19-aldehyde semi-acetal, which with alkali formed 19-norcorticosterone; photolysis of the 11-nitrite of this (CVII) produced the 19-oxime, which on removal of the oxime group by a known procedure[242,243] yielded 19-noraldosterone (CVIII). 17α-Hydroxy-19-noraldosterone was prepared analogously[244,245].



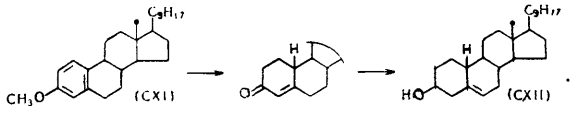
(ii) According to the patent literature[246-248], reductive amination of 11β-hydroxy-19-norprogesterone with butylamine gave the amine (CIX), which by chromium(VI) oxide oxidation and photolysis was converted into a 19-norconamine derivative; this was reduced with lithium tetrahydroaluminate, subjected to Hofmann degradation, and

treated with potassium hydroxide to obtain the 11β,18-oxide (CX). Successive oxidation of the 3-hydroxy-group with chromium(VI) oxide, of the 20(21)-double bond with osmium tetroxide, and of the 11β,18-oxide ring with ruthenium tetroxide gave the 11,18-lactone, which was brominated and then dehydrobrominated to obtain a double bond in the 4-position; formation of a hydroxyacetyl side-chain by hydrolysis and chromium(VI) oxide oxidation and, finally, reduction of the lactone group with lithium tetrahydroaluminate gave 19-noraldosterone (CVIII).

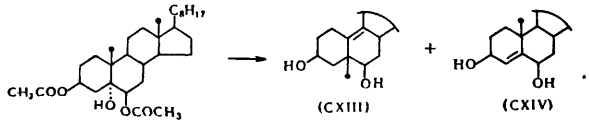


5. DERIVATIVES OF 19-NORCHOLESTEROL AND OTHER STEROIDS

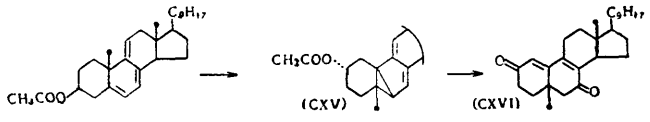
The simplest member of this series of compounds, 19-norcholesterol (CXII), has been prepared by Birch reduction of (CXI) to the 4-en-3-one and potassium tetrahydroborate reduction of the enol acetate. 7-Dehydro--19-norcholesterol has been prepared in an analogous manner[181,249]:



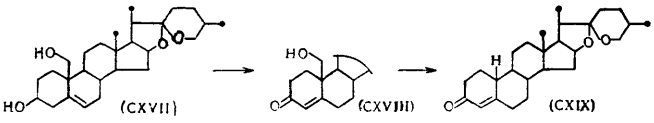
The Westphalen rearrangement is widely used for preparing derivatives of 19-norcholestane; it takes place by a mechanism similar to that of the Wagner–Meerwein rearrangement, and is accomplished by the action of a mixture of acetic anhydride and sulphuric acid or potassium bisulphate on 3,5,6-triols. This reaction has been employed to convert cholestane-3β,5α,6β-triol 3,6-diacetate into the so-called "Westphalen's diol", 5β-methyl-19-norcholest-9(10)-en-3β,6β-diol (CXIII);[250,251] in addition to a 61% yield of this compound, the reaction also gave the normal dehydration product (CXIV) in 9% yield. Under the experimental conditions, therefore, isomerism greatly predominates over dehydration[252]. The structure of Westphalen's diol was proved by spectroscopic methods and by numerous chemical reactions[253–263]. 6β-Acetoxy-5α--hydroxy-3β-methoxycholestane[264,265] and 3β-acetoxy-6β--fluoro(chloro, bromo)-5α-hydroxycholestane[266] have also been subjected to the Westphalen rearrangement.



Derivatives of 19-norergostane containing a 5-methyl group can be obtained by photochemical rearrangements. Thus photolysis of dehydroergosterol acetate produces the compound (CXV), which has been converted in three steps into the diketone (CXVI). Analogous treatment of the acetic ester of dehydrolumisterol (the $C_{(10)}$-epimer of dehydroergosterol) gives the isomer of the ketone (CXVI) with a 5α-methyl group; this photochemical rearrangement is thus fully stereoselective[267,268].

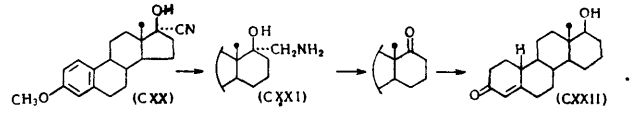


Ruscogenin (19-hydroxydiosgenin, a steroid sapogenin isolated from *Ruscus aculeatus*) (CXVII) undergoes Oppenauer oxidation to form the 4-en-3-one (CXVIII), which with alkali yields 19-nor-22α-spirost-4-en-3-one (CXIX), the first known 19-norsapogenin[269]:



6. 19-NOR-*D*-HOMOSTEROIDS

This class of compound includes 19-nor-*D*-homotestosterone, which has been prepared by total and partial synthesis, and certain of its derivatives. 19-Nor-*D*-homotestosterone (CXXII) has been obtained by partial synthesis from natural oestrone methyl ether cyanohydrin (CXX); lithium tetrahydroaluminate reduction of this produces the amine (CXXI), which on treatment with nitrous acid undergoes ring expansion to form the *D*-homosteroid. Successive reduction with sodium tetrahydroborate and lithium in liquid ammonia gives (CXXII), which has a ratio of anabolic to androgenic activity of 6 (testosterone = 1)[270]:



Racemic 19-nor-*D*-homotestosterone has been synthesised from 1,2,3,4-tetrahydro-6-methoxy-1-oxonaphthalene; the vinyl-substituted alcohol obtained from this was condensed with dihydro-2-methylresorcinol to give the diketone (CXXIII), which was cyclised to a chrysene derivative and the latter hydrogenated to the 14α-dihydro-compound (CXXIV). Reduction of the 17a-keto-group with lithium tetrahydroaluminate and of ring *A* with lithium in liquid ammonia produced (±)-19-nor-*D*-homotestosterone (CXXII), from which the 17α-methyl and 17aα-ethyl derivatives

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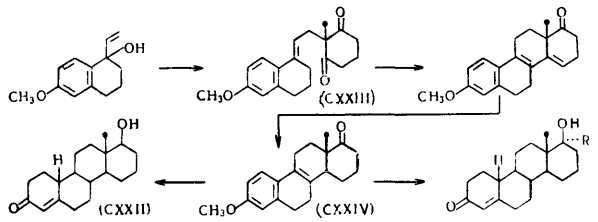
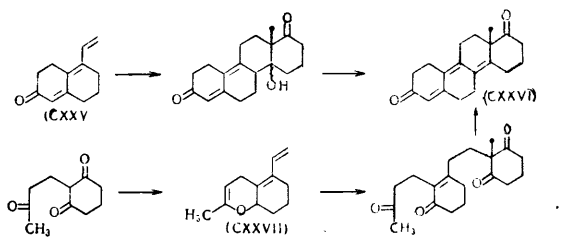
were prepared. All these compounds have a high index of anabolic and androgenic activity, *e.g.* 3.7 for (CXXII), and 11.3 for its phenylpropionate[271-275].



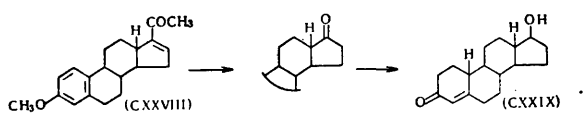
19-Nor-*D*-homosteroids have also been prepared by another procedure. The trienone (CXXV), obtained from methoxytetralone, was condensed with dihydro-2-methylresorcinol under the conditions of the Michael reaction to give 14ξ-hydroxy-19-nor-*D*-homoandrosta-3,9-diene--3,17a-dione. Dehydration of this with toluene-*p*-sulphonic acid produced the trienedione (CXXVI).[276,277] Compound (CXXVI) has been prepared also from the condensation product of dihydroresorcinol with methyl vinyl ketone, which was converted in three steps into the triene (CXXVII); condensation of this triene with dihydro-2-methylresorcinol gave a tetraketone, which under the influence of a pyridine–diethylamine mixture underwent double cyclisation to the trienedione (CXXVI).[278]



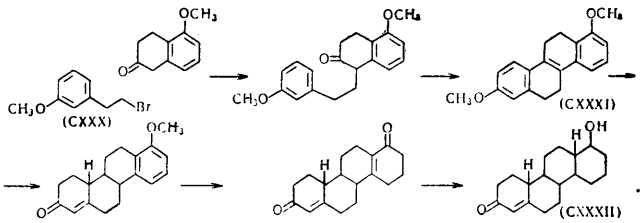
7. 18,19-DINORSTEROIDS

18,19-Dinorsteroids of the androstene, *D*-homoandrostane, and pregnane series have been prepared.

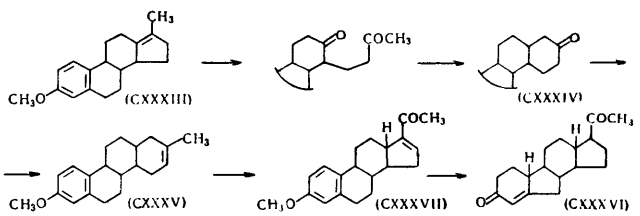
18,19-Dinortestosterone (CXXIX) has been obtained from the compound (CXXVIII), which is an intermediate in the synthesis of 18,19-dinorprogesterone (see below). Removal of the side-chain of this compound gave the 17-ketone, which on successive reduction with lithium tetrahydroaluminate and lithium in liquid ammonia formed (CXXIX); this has no androgenic or anti-oestrogenic activity[221].



A procedure has been developed for the total synthesis of 18,19-dinor-*D*-homotestosterone. Alkylation of methoxytetralone with the bromide (CXXX) produces a dimethoxy--ketone, which can be cyclised to the dimethoxychrysene derivative (CXXXI). Reduction of the central double bond with sodium in butanol and of ring *A* by the Birch method gave the compound with an aromatic *D* ring; this was converted into its ethylene ketal, ring *D* also reduced by the Birch method, the reduction product hydrolysed, and the resulting diketone reduced at the double bond and the keto--group in ring *D* to give 18,19-dinor-*D*-homotestosterone (CXXXII); this has neither androgenic nor anabolic activity[279-282]. The 11α-hydroxy-analogue of (CXXXII) has also been prepared by total synthesis; it has weak androgenic activity[283].



18,19-Dinorprogesterone (CXXXVI) has been prepared by heating oestradiol with boric acid to give (CXXXIII), which is ozonised to the diketone, and the *D*-homo-ketone (CXXXIV) obtained from this in three stages. Reaction of (CXXXIV) with methylmagnesium iodide and subsequent dehydration produces (CXXXV), which on ozonolysis to the corresponding dialdehyde followed by cyclisation gives the pregnane derivative (CXXXVIII); this on Birch reduction and oxidation of the resulting 20ξ -hydroxy-compound with chromium(VI) oxide yields (+)-18,19-dinorprogesterone (CXXXVI), which has no gestagenic activity[284-287]. Racemic 18,19-dinorprogesterone (CXXXVI) and its 14α-hydroxy--analogue have been prepared by total synthesis using a modified Sarett procedure; these compounds have less than 2% of the gestagenic activity of progesterone[288].



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2,4,6-TRICHLORO-1,3,5-TRIAZINE (CYANURYL CHLORIDE) AND ITS FUTURE APPLICATIONS

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I. INTRODUCTION

The chemistry of 2,4,6-trichloro-1,3,5-triazine† (cyanuryl chloride)[1-5] formed the subject of a section in the comprehensive monograph "s-Triazines and Derivatives"[6], which reviewed work, published up to 1954, on the preparation, reactions, and applications of the compound. The problem of the reactivity of cyanuryl chloride and other halogenated derivatives of triazine was not discussed in the monograph.

Although the chemistry of cyanuryl chloride has been intensively developed since then, only one review paper in Japanese, covering the literature up to 1956, has dealt with this question[7]. It describes the synthesis of triazine derivatives from cyanuryl chloride, and examines some relations between the nature of the reactants and their reactivity. This review does not cover the practical application of cyanuryl chloride and the products obtained from it.

The chemistry of cyanuryl chloride has not been reviewed in the Soviet literature, and it is therefore opportune and useful to report progress in this field.

A great achievement is the production of a new type of dyes — the reactive dyes[8-28] — based on cyanuryl chloride. Their molecules contain active chlorine atoms combined with the triazine ring, and during dyeing react with the hydroxy- or amino-groups of the fibre. This results in the formation of a chemical compound between the fibre and the dye, which is of ether type in the case of cellulose and of amide type with wool and other fibres containing primary or secondary amino-groups. The resulting dyeings are distinguished by their brightness and purity of colour and by exceptionally high fastness to wet treatments, and the dyes themselves by simplicity of application and relative cheapness, which gives them an advantage over other groups of dyes.

Cyanuryl chloride is of great value for agricultural needs: especially during recent years numerous derivatives have been synthesised which act as insecticides, fungicides, and week-killers[29-37], some of which have already been used in agriculture. The most effective are compounds containing active chlorine atoms combined with triazine, in particular 2-chloro-4,6-bisdimethylaminotriazine, and also dichloro-derivatives of triazine.

Recently compounds have been obtained from cyanuryl chloride which inhibit the growth of tumors, and this may prove invaluable in the treatment of cancer[38-41]. Other drugs required in medicine are synthesised on the same basis, for example antitubercular[42,43] and trypanocidal[44-49] preparations.

Cyanuryl chloride is of equal value for the synthesis of many other substances required in various branches of the economy. Thus certain sulphur-containing triazine derivatives obtained from cyanuryl chloride act as antioxidants[50], plasticisers[51], and vulcanisation accelerators[53] in the rubber industry. Other preparations have great importance as textile auxiliaries, especially as finishing[54] and brightening[55,56] agents. In the synthetic dye industry cyanuryl chloride is employed not only for the synthesis of reactive dyes, on which more than a hundred patents have been taken

† Since the present review is concerned only with derivatives of 1,3,5-triazine, the numerical locants will be omitted, and the molecule referred to simply as "triazine".

out (during 1957–1961)[57], mainly by Ciba and I. C. I., but also in the manufacture of direct (especially green)[58,59], vat (Ref. 59, p. 1021), and several other dyes[52,60-62].

The diversity of the fields of application of cyanuryl chloride is due to its distinguishing feature — the presence in its molecule of three active chlorine atoms, which can be replaced one by one. The successive substitution of the chlorine atoms when cyanuryl chloride reacts with various compounds enables a multitude of the most diverse substances to be obtained.

II. REACTIVITY OF CYANURYL CHLORIDE AND OF TRIAZINE

The ease of replacement of the chlorine atoms in cyanuryl chloride and its partial substitution products, *i.e.* di- and mono-chlorotriazines, is determined both by the nature of the nucleophilic reagent and by the number and nature of the substituents linked to the triazine ring. Thus the reactivity of cyanuryl chloride itself and of many of its monosubstituted derivatives is roughly equal to that of oxychlorides[63] or acid chlorides of certain carboxylic acids[64]; in disubstituted derivatives it in general approximates in reactivity to the alkyl halides, although reactivity depends on the nature of the substituents.

The reactivity of cyanuryl chloride and of other chlorinated triazines is governed also by the specific structure of the ring, which is usually represented as a six-membered cyclic system (I) consisting of alternating nitrogen and carbon atoms linked by alternating single and double bonds, resembling formally the benzene ring

(I)

While comprising a six-membered ring with a closed system of π electrons, triazine is distinguished from the benzene system by the characteristic presence of six unpaired electrons on the nitrogen atoms, which form part of the general system. It is probably this which is responsible for the peculiarities of the triazine system, and distinguishes it from the usual aromatic system of benzene. The increased electron density on the nitrogen atoms compared with the carbon atoms‡ in the triazine ring destroys the electronic symmetry, resulting in diminished stability compared with benzene and the capacity for addition reactions, while *C*-halogenated triazines, especially cyanuryl chloride, can undergo substitution reactions. The instability of the unsubstituted symmetrical triazine ring is shown, for example, in its hydrolysis, especially in the presence of mineral acids, when reaction is almost instantaneous, formic acid and ammonia being produced[66,67]. Ring-opening occurs also on treatment of triazine with sodamide or a primary or secondary amine, the products being in the first case sodium cyanide and ammonia, and in the second a substituted formamidine[6]. Weakening and rupture of a C–N bond in triazine occur also on treatment with aluminium chloride[6].

The instability of triazine has prevented it from being obtained by the removal of substituents from the triazine ring by the usual methods[6]. This also constitutes an important distinction from benzene and other aromatic hydrocarbons, which can be prepared[68] in this way.

In contrast to benzene, triazine can undergo addition reactions. With hydrogen chloride, for example, it yields the addition product $2C_3H_3N_3.3HCl$,[67] and with silver[67] and mercury[69] salts the compounds $AgNO_3.2C_3H_3N_3$, $AgNO_3.C_3H_3N_3$, and $HgCl_2.C_3H_3N_3$. Even halogen adds on at 0° in carbon tetrachloride[70].

Triazine does not undergo catalytic hydrogenation[70]. It is a catalyst poison, even traces of it poisoning the catalyst in the hydrogenation of cyclohexene.

Owing to the diminished electron density on the carbon atoms, triazine is incapable of the electrophilic substitutions — nitration and sulphonation — characteristic of benzene. For the same reason it has not proved possible to prepare *C*-nitro-derivatives by replacing a chlorine atom in cyanuryl chloride by a nitro-group or by oxidising amino-derivatives of triazine[7].

The diminished electron density of the carbon atoms in triazine explains the great mobility of the halogen atoms in its halogenated derivatives, in particular of chlorine in cyanuryl chloride, which distinguishes the latter fundamentally from chlorobenzenes. Replacement of one or two chlorine atoms in cyanuryl chloride by electron-donor groups should increase the electron density on the triazine carbon atoms, and thereby diminish the activity of the remaining chlorine atoms, as actually occurs.

Thus replacement of the chlorine atoms in cyanuryl chloride by amino- or hydroxy-groups takes place in stages[64,71,72], and this is a consequence of the levelling out of electron density in the triazine, *i.e.* of its increase on the carbon atoms due to entry of an electron-donor substituent. A similar phenomenon is observed when one or two chlorine atoms are replaced by alkoxy-groups[73], as a result of which the C–Cl bond becomes more stable, and the chlorine atoms become less active. A CHN_2 group has a similar but less clearly defined effect[74].

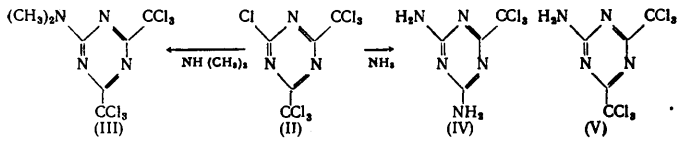
Study of the hydrolysis of 6-alkylamino-, 6-alkoxy-, and 6-alkylthioderivatives of 2,4-dichlorotriazine showed the alkylamino-derivatives to be the most stable; in the other groups of derivatives the chlorine atoms were more mobile[75]. The hydrolysis rate constants for these derivatives show that a compound is more stable (the chlorine is less mobile) the more readily the XAlk group donates electrons.

If, on the other hand, we assume that one or two chlorine atoms in cyanuryl chloride have been replaced by groups which can attract electrons no less strongly than does chlorine, *i.e.* by groups capable of diminishing the electron density on the carbon atoms in triazine and thereby promoting nucleophilic substitution, in this case substitution would have no deactivating influence on the reactivity of the remaining one or two chlorine atoms.

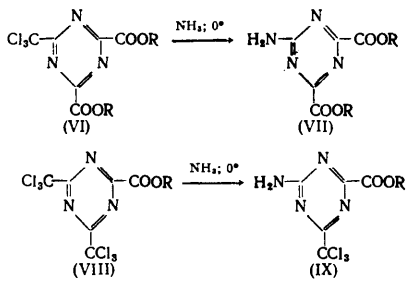
In fact, if two chlorine atoms in cyanuryl chloride are replaced by CCl_3 groups, which can be readily exchanged for nucleophilic substituents[76,77], deactivation of the remaining chlorine is not observed. Thus when the compound (II) reacts with dimethylamine, the chlorine is replaced even

‡ The non-uniform distribution of electron density is confirmed by calculation, which gives relative values of 1.179 and 0.821 on nitrogen and carbon respectively[65].

at 0°, with formation of (III).[78] Reaction of (II) with ammonia yields (IV), but (V) is not formed; this indicates that a group can readily undergo substitution if it itself exerts no deactivating influence on the other substituent:



It is probable that the ester group likewise does not deactivate substitution in the triazine ring[7]. Ammonia acts on (VI) to give (VII) even at 0°, and in the same way (VIII) yields (IX).



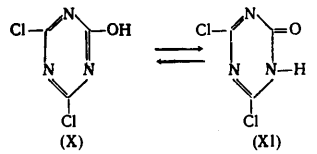
Replacement of a chlorine atom in cyanuryl chloride by a cyano-group probably does not diminish the activity of the remaining chlorine atoms, for, being linked to triazine, the cyano-group itself develops sufficient mobility. 2,4,6-Tricyanotriazine hydrolyses readily[79], and even in the cold is rapidly decomposed by water into hydrogen cyanide and cyanuric acid.

It follows that the nature and extent of the influence of substituents in the triazine ring on the activity of chlorine depend on their electronegativity. However, few data are yet available on this point, and the influence of substituents in the triazine ring can be assessed only qualitatively, by analogy with systems which have been studied more thoroughly, for example substituted bromobenzene. In the reaction of piperidine with *para*-substituted *o*-bromonitrobenzenes the substituent groups arrange themselves in the following sequence of diminishing deactivating effect on replacement of the bromine: $NH_2 > OH > N(CH_3)_2 > > OC_2H_5 > OCH_3 > CH_3 > C_4H_9^t > H > COOH > Cl, Br$.[80]

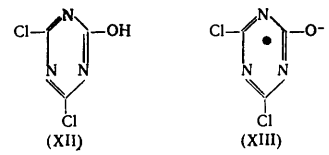
The activity of chlorine attached to a triazine carbon atom is influenced not only by the degree of electronic saturation of the substituent but also by whether or not it contains a reactive hydrogen atom.

Thurston *et al.*[72] noted that chlorine atoms in 2,4-dichlorotriazines are more active when a 6-monoalkylamino--group rather than a 6-dialkylamino-group is present. They explain this phenomenon by the fact that, if the substituent contains hydrogen, it can act as a hydrogen-donor in the triazine or the tautomeric dihydrotriazine. The attacking molecule, for example water (in hydrolysis), forms a hydrogen bond with the latter, thereby facilitating attack on an adjacent C–Cl bond. Hydrogen-bond formation is impossible in molecules of 2,4-dichloro-6-dialkylamino--1,3,5-triazines.

Precise data are lacking for hydroxy-derivatives. Wegmann[81] has reported the preparation of 2,4-dichloro-6-hydroxytriazine (X), which exhibits very little activity, undergoing reaction only at high temperatures, with the participation of only one chlorine atom. It is assumed that the low reactivity of this compound is due to its ability to pass into the tautomeric form (XI) with loss of its "aromatic" properties. As a result, the chlorine atoms which it contains differ in activity.



Matsui and Sakamoto[63] made a careful study of the hydrolysis of cyanuryl chloride in alkaline medium, and concluded that 2,4-dichloro-6-hydroxytriazine is fairly reactive: one of its chlorine atoms is very readily hydrolysed, and both chlorine atoms can be replaced by aniline under mild conditions. The sodium salt of this compound is stable, and is not hydrolysed at 0–5° even in the presence of strong alkali; its chlorine atoms cannot be replaced by aniline in alkaline medium. The diminished reactivity of the sodium salt of dichlorohydroxytriazine is explained by the difference in electron density on the triazine ring in the compounds (XII) and (XIII), *i.e.* by the different effects of the substituents OH and O^- on the activity of the chlorine.



As a result of the lack of agreement between observations made by different investigators, we may regard the reactivity of 2,4-dichloro-6-hydroxytriazine as an open question, especially in view of the fact that the Japanese workers did not succeed in isolating either the compound (XII) or 2-chloro-4,6-dihydroxytriazine. When an attempt was made to obtain these compounds by acidifying solutions of their sodium salts, only cyanuric acid was formed. The compound obtained by Wegmann was not characterised, nor was its mode of synthesis described.

The activity of chlorine atoms in triazine derivatives is affected by various substituents even when the latter are not directly linked to the triazine but are present in an aromatic ring combined with the latter[75,82]. Koopman[75] found that *para*-substituents in 2,4-dichloro-6-phenyltriazines could be arranged in the following sequence according to their acceleration of hydrolysis: $OCH_3 < SCH_3 < < H < SO_2CH_3 < NO_2$. The results do not contradict Hammett's rule if Jaffé's values[83] of σ are accepted for the above substituents.

Other investigators[84,85] have observed the effect of substituents, as a function of their polarity, on the reactivity of arylaminochlorotriazines.

III. REACTIONS OF CYANURYL CHLORIDE

Cyanuryl chloride is characterised mainly by reactions involving substitution by nucleophilic reagents. In contrast to triazine itself, reactions involving cleavage of the ring are not characteristic of cyanuryl chloride, and addition reactions are quite unknown.

Although many reactions involving substitution in cyanuryl chloride and other chlorinated triazines have been described, little work has been done on their mechanism. Only in a few cases has it been shown that the main reaction of cyanuryl chloride with nucleophilic reagents takes place by an S_N2 mechanism. [7,85]

1. Hydrolysis

Interest in the hydrolysis of cyanuryl chloride and of its partial conversion products is due mainly to its being a side-reaction in the preparation of several products of practical importance. Sometimes the hydrolysis of these derivatives is utilised for the preparation of triazine derivatives containing hydroxy-groups. For example, a quantitative yield of ammelide (2-amino-4,6-dihydroxytriazine) is obtained[87] by the hydrolysis of 2-amino-4,6-dichlorotriazine, which is readily prepared from cyanuryl chloride and ammonia[72,86]. Ammeline (2,4-diamino-6-hydroxytriazine) is obtained[88] in a similar manner from 2,4-diamino--6-chlorotriazine[72]. Complete hydrolysis of cyanuryl chloride itself yields cyanuric acid (2,4,6-trihydroxytriazine $\rightleftharpoons$ 2,4,6-trihydro-2,4,6-trioxotriazine). The most convenient method for its preparation is to boil cyanuryl chloride with glacial acetic acid[6] for 1 h, when the yield is 95%.

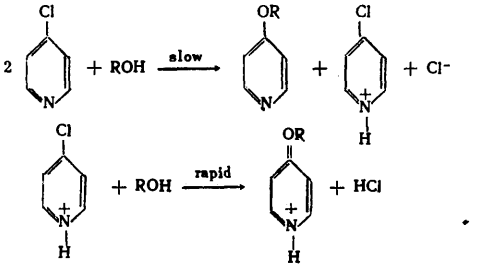
The hydrolysis of cyanuryl chloride and other chlorinated triazines, which usually takes place in aqueous medium or in a mixture of water with an organic solvent, is considerably accelerated by elevated temperatures and the presence of alkali. Opinions differ concerning the effect of acids. Only cyanuric acid has been isolated among the products of the acid hydrolysis of cyanuryl chloride[63,89,90].

Fierz-David and Matter[64] found that cyanuryl chloride was stable in water at 0° for 12 h, but it was rapidly hydrolysed even at room temperature. The experiments were made in the presence of calcium carbonate in an apparatus which enabled the course of hydrolysis to be followed from the amount of carbon dioxide evolved. These workers gave no data on the complete hydrolysis of cyanuryl chloride or its intermediate products.

Matsui and Sakamoto[63] studied the hydrolysis of cyanuryl chloride in aqueous acetone medium at 15° with and without addition of acid, but were unable to follow the different stages in the process owing to the rapid breakdown of the intermediate compounds to cyanuric acid. Previous addition of hydrochloric acid was found to slow down the initial stage of hydrolysis, but to increase the rate of hydrolysis of the intermediate compounds, which for this reason could not be isolated. Their presence was established only from the shape of the hydrolysis curve.

In a study of the hydrolysis of dichlorotriazines in aqueous acetone medium Koopman[75] found the same rate constant for hydrolysis of the first chlorine atom in 2-butoxy-, 2-butylthio-, and 2-phenyl-4,6-dichlorotriazines, whether or not the original mixture had first been acidified with nitric or sulphuric acid to pH 1. From this he concluded that hydrogen ions do not influence the rate of hydrolysis of chlorinated triazines.

However, Koopman's views are at variance with the concept of the acid catalysis of nucleophilic substitution reactions in nitrogeneous heterocyclic compounds (containing halogen attached to a carbon atom conjugated with the ring nitrogen atom)[47,48,91], a particular case of which is provided by the autocatalysis of hydrolysis and alcoholysis[92,93]

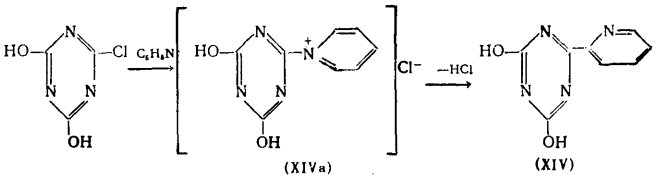


As a result of this, halogenated "aromatic" heterocycles are extremely sensitive to moisture, hydrolysis yielding the hydrogen halide, which accelerates further decomposition. A similar phenomenon is observed with halogenated triazines.

In contrast to acid hydrolysis, for which occurrence of the reaction in stages has not been established, with alkaline hydrolysis the existence of intermediate compounds has been shown, and they have been isolated. Fierz--David[64] was the first to report the formation of 2-chloro--4,6-dihydroxytriazine, a product of the incomplete hydrolysis of cyanuryl chloride with 10% caustic soda at 100°. The third chlorine atom is replaced only when the temperature is raised to 125°. These results have since been repeated many times and reported in the literature[6,7,63].

Wegmann reported[81] that the structure of 2,4-dichloro--6-hydroxytriazine — a product of the incomplete hydrolysis of cyanuryl chloride — had been established analytically, and that the substance was extremely unstable, liable to explosive decomposition when dry, but no information on its method of preparation or its properties has yet been published.

The presence of 2-chloro-4,6-dihydroxytriazine among the products of the partial alkaline hydrolysis of cyanuryl chloride was proved by Saure[71], who converted this compound into 2,4-dihydroxy-6-2′(or 4′)-pyridyltriazine (XIV), the reaction being assumed to proceed as follows



Japanese workers[63] have made the most detailed study of alkaline hydrolysis. They have been the first to isolate and analyse the sodium salts of 2,4-dichloro-6-hydroxytriazine and 2-chloro-4,6-dihydroxytriazine. In contrast to the hydroxy-compounds themselves, these salts are characterised by stability to alkalis. In the presence of acids, they are first converted into the hydroxy-compounds, which are rapidly hydrolysed to cyanuric acid.

The sodium salt of 2,4-dichloro-6-hydroxytriazine was obtained by the hydrolysis of cyanuryl chloride at room temperature with solutions of sodium bicarbonate or carbonate in the proportion of at least 2 moles per mole of cyanuryl chloride, as well as in the presence of a slight excess of sodium hydroxide at 0–5°. This salt is stable, and when

dry can be stored for a long time; in aqueous solution at room temperature no change in acidity is observed for several days.

The monosodium salt of 2-chloro-4,6-dihydroxytriazine has been obtained by the hydrolysis of cyanuryl chloride or its monohydroxy-derivative in the presence of excess of caustic soda at 15–40°. This salt is still more stable to the prolonged action of alkali. Its hydrolysis in the presence of caustic soda begins at 80–90°. On hydrolysis in the presence of an insufficient quantity of neutralising reagent, the solution gradually becomes acid, with the formation of cyanuric acid.

The hydroxy-derivatives themselves could not be isolated. Their existence was proved by the formation of 2,4-dianilino-6-hydroxytriazine (XV) and 2-anilino-4,6-dihydroxytriazine (XVI) by the action of aniline on the sodium salts of the hydroxy-derivatives in faintly acid medium. Since (XVI), in contrast to (XV), is soluble in aqueous alkali, the amounts of the original hydroxy-compounds could be determined in the mixtures formed by hydrolysis under various conditions.

2. Reactions with Amines

The interaction of cyanuryl chloride with amines shows a stepwise course still more clearly than does its hydrolysis. However, the generally accepted empirical rule, according to which the first chlorine atom in cyanuryl chloride is replaced at 0°, the second at 30–50°, and the third at 90–100°, cannot be regarded as of general validity, although it is applicable to many reactions occurring in aqueous medium[42,44–46,64,94,95].

In several cases the second chlorine atom can be replaced even at 0°.[64] This occurs, for example, with sulphanilic acid and several other amino-sulphonic acids of the benzene and naphthalene series. Several amines can react with all three chlorine atoms at 0°.[96] Relatively inactive amines, for example those of the anthraquinone series, which do not contain sulphonato-groups, react in anhydrous solvents (usually nitrobenzene) above 100°, when a stepwise course of the reaction is not observed, and sometimes only two chlorine atoms can be replaced[64]. In such cases reaction must be carried out in boiling phenol in order to substitute the third chlorine atom (Ref. 59, p. 1021). Several amines do not react at all with cyanuryl chloride at 100°.[6]

The complete reaction of cyanuryl chloride with primary and secondary aliphatic and aromatic amines yields substituted melamines; melamine itself (2,4,6-triaminotriazine) is obtained by the action of ammonia on cyanuryl chloride. The reaction can take place in stages depending on the conditions: 2-amino-4,6-dichlorotriazine is formed in cold ethereal solution[72,87], 2,4-diamino-6-chlorotriazine in aqueous solution at room temperature[72], and melamine at 100° under pressure[97,98].

The possibility of stepwise reaction between cyanuryl chloride and ammonia was shown long ago by Diels[87] in the synthesis of trisubstituted triazines by various methods. Three different amines — NH_3, CH_3NH_2, and $C_2H_5NH_2$ — were made to react successively with cyanuryl chloride at 0°, then at 20–60°, and finally at 100°. Changes in the sequence in which the reagents were made to react yielded in all cases the same substance, which proves the stepwise character of the process.

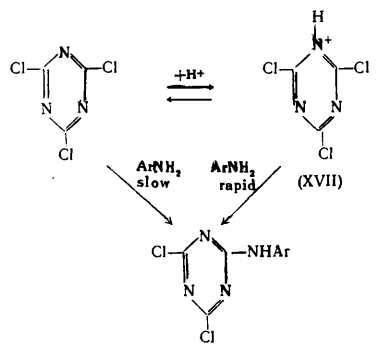
The reaction between cyanuryl chloride and amines occurs in stages, as does hydrolysis, as a result of the influence of the substituent in the triazine on the activity of the chlorine atoms which are present. Substituents having a greater tendency to donate electrons increase the electron density of the triazine ring, the C–Cl bond becomes more stable, and as a consequence the chlorine becomes less mobile.

Apart from substituents, the nature of the amine, determined both by its basic strength and by the steric factor, affects its reaction with chlorinated triazines. Of course, amines which are weak bases, for example aromatic amines containing negative substituents (2,4-dinitroaniline), react less vigorously than do stronger bases with chlorinated triazines. The ease of reaction with such amines as ethyleneimine[96], morpholine[38,39,99], and piperidine[71] is due to the absence of steric hindrance[6]. With these amines all the chlorine atoms can be replaced after a short time at 0–25°. Nevertheless, amines with even slight steric hindrance, such as diethylamine and iminodipropionitrile, form only monoamino- and diamino-derivatives at 25°.

Substitution of chlorinated triazines by amines is greatly affected by the nature of the solvent. The reaction is accelerated in polar solvents, especially in water, if the solubility of the amines permits their use. Reaction is more rapid in acetonitrile than in benzene[96], and the third chlorine atom in triazine can sometimes be replaced only in phenol (Ref. 59, p. 1021), as already mentioned.

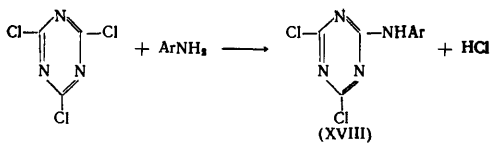
The reaction between chlorinated triazines and amines is usually carried out in the presence of an acid-binding agent, for example caustic soda, sodium carbonate or bicarbonate, or a tertiary amine, sometimes the amine used for the reaction.

Sometimes the reaction is catalysed by acids, as with other nitrogen-containing heterocyclic systems[47,48,91,100]. For example, the reaction of 2,4-diamino-6-chlorotriazine with aniline is accelerated by the presence of hydrochloric acid, but slowed down on addition of caustic soda[91]. In the presence of a large excess of acid, however, hydrolysis takes place at the same time. A similar phenomenon is observed with other aromatic amines and chlorinated triazines[47], sulphuric and tartaric acids also having a catalytic effect[91]. This phenomenon is explained by the diminution in electron density on the carbon atom of triazine caused by formation of an "ammonium"[91] or a triazinium ion[22] (XVII), which facilitates attack on the carbon atom by nucleophilic reagents:



Bitter and Zollinger[101,102] studied the kinetics of the reaction between cyanuryl chloride and nucleophilic reagents (aromatic amines) in a non-polar medium (benzene), and found that in the case of primary amines the reaction

does not follow a simple second-order law. Owing to autocatalysis, an induction period appears, the final reaction product (XVIII) accelerating the process:

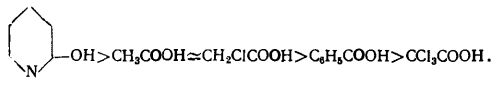


(XVIII)

The catalytic action of (XVIII) is due to the presence of the hydrogen atom in the NHAr group, as a result of which this compound functions as an acid. If the substituent group does not contain hydrogen, as in the case of *NN*-dialkylamino-derivatives, the reaction is not accelerated. This explains the absence of autocatalysis in substitution by secondary amines.

Other workers[103] have also observed autocatalysis in reactions of various 2-amino-4,6-dichlorotriazines with primary aromatic amines.

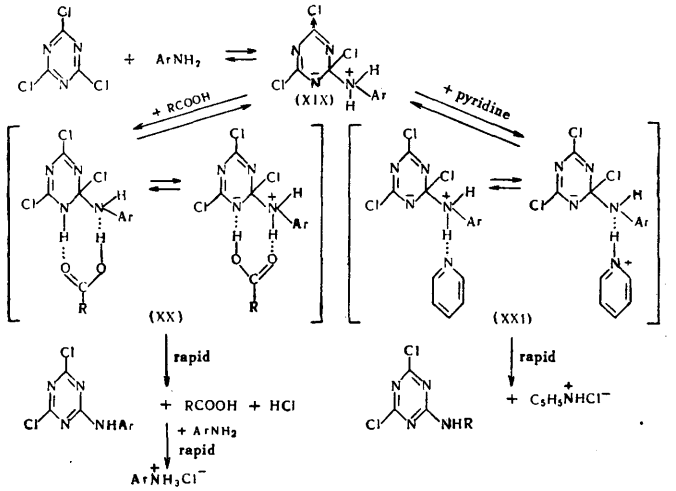
Several organic acids also catalyse the reaction between chlorinated triazines and amines in non-polar solvents[102]. Their effect is not directly related to their dissociation constant. These acids can be arranged in the following sequence according to the magnitude of their effect on the reaction velocity



Phenol, *o*- and *p*-nitrophenols, and picric acid show practically no catalytic effect.

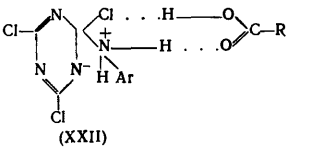
The reaction of cyanuryl chloride with arylamines is accelerated also by bases such as pyridine and triethylamine[22].

Bitter and Zollinger have shown[22] that substitution is rather more rapid with *NN*-dideuteroaniline than with aniline in the presence of acetic acid [$k_H/k_D = 0.95$] and rather slower in the presence of pyridine [$k_H/k_D = 1.04$].



All of these results suggest that an intermediate product (XIX) is formed, the breakdown of which is accelerated both by pyridine or the amine (proton–acceptors) and by bifunctional catalysts such as carboxylic acids and pyrid-2-one[104]. Reaction proceeds via the complexes (XX) and (XXI). The bifunctional compounds then act, on the one hand, as Brønsted acids (proton–donors), activating the nitrogen in the α position of the heterocycle, and on the other hand as proton–acceptors (the carbonyl oxygen or the nitrogen in the pyrid-2-one), drawing off hydrogen from the amine[22]).

The hypothetical formation of an intermediate complex ion

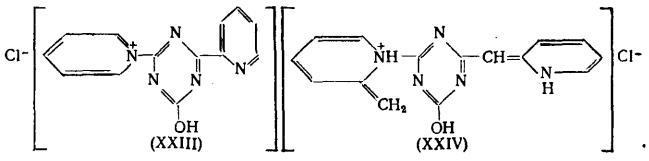


(XXII)

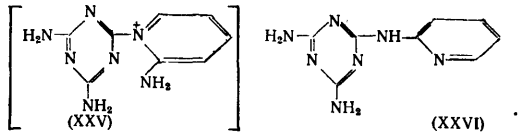
is improbable, for the hydroxy-proton of the acid would then facilitate the elimination of chlorine. However, this is inconsistent with the fact that replacement of the chlorine atom in 1-chloro-2,4,6-trinitrobenzene, which is similar in reactivity to cyanuryl chloride, is not catalysed by carboxylic acids.

Cyanuryl chloride and other chlorinated triazines react not only with aliphatic and aromatic primary and secondary amines containing one functional group[35,38,39,72,99,105] but also with aminophenols[106], arylsulphonylarylamines[43], and aminoarenesulphonamides[107]. Similar behaviour is shown by compounds in which the amino-group is not attached to carbon, such as arenesulphohydrazides.[108], sulphonamides[109], and hydrazines[110], salts of urea[51] and its derivatives, as well as thiourea and its derivatives[51]. Heterocyclic amines have also been employed in this reaction, such as 8-amino-6-methoxyquinoline[42], 4,6-diamino-2-methylquinoline[111], *N*-3-aminopropylpiperidine[112], 2-aminopyridone[113], and 4,6-diaminoquinaldine[49], as well as piperazine, piperidine, and morpholine[38,39,99,113].

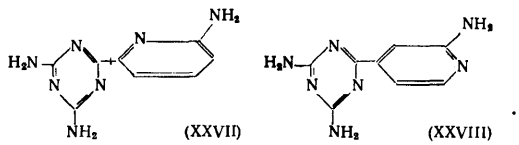
Tertiary amines, although usually employed as neutralising agents in reactions between chlorinated triazines and compounds containing a mobile hydrogen atom, react in several cases with chlorotriazines to form quaternary ammonium salts[114]. Analogous compounds are formed also with pyridine (see XIVa)[71]; under different conditions (XXIII) is formed[71]. If pyridine is replaced by 2-methylpyridine, the compound (XXIV) is obtained[115].



Reaction of 2-aminopyridine with 2,4-diamino-6-chlorotriazine involves the intermediate formation of a quaternary ammonium salt (XXV), the final product of the reaction being 2,4-diamino-6-2′-pyridylaminotriazine (XXVI)[113].



The isomeric compounds (XXVII) and (XXVIII) are formed as byproducts



Numerous reactions of cyanuryl chloride and other chlorinated triazines with more complicated amines are known, the latter including aminoazo-compounds, aminoanthraquinones, and other cyclic compounds of practical value [52,57].

3. Reactions with Alcohols and Phenols

Cyanuryl chloride can react with alcohols [73] in stages. Owing to the weaker deactivating influence of the OAlk group in comparison with NHAlk, NHAr, and NAlkAr, however, the stepwise character of the process is less clearly marked than in the reaction with amines. The stepwise character of the reaction with phenols [116] is still less strongly developed, for the same reason.

Replacement of chlorine by OAlk is easily accomplished by treating cyanuryl chloride with alkoxides [117-119] or with alcohols in the presence of bases [117]. Depending on the amount and nature of the alkaline reagent, the process can occur in stages [73]; it is preferable to use sodium bicarbonate, carbonate, or hydroxide. However, in the presence of caustic soda the reaction may be accompanied, even on cooling, by replacement of all the chlorine atoms. For example, the gradual addition of a concentrated solution of sodium hydroxide to a cooled suspension of cyanuryl chloride in allyl alcohol [120] may yield triallyloxytriazine.

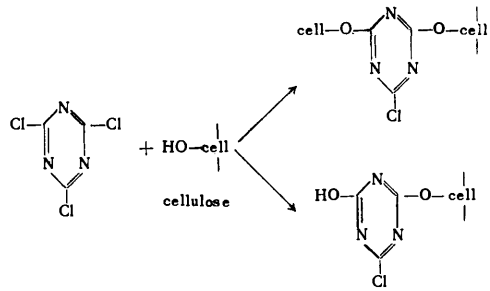
The stepwise interaction of cyanuryl chloride with various alcohols has been studied [121] in the presence of calcium carbonate between 0° and 35°, and the successive formation of mono-, di-, and tri-alkoxy-derivatives of triazine has been established. Measurement of the quantity of carbon dioxide evolved gave the rate of the process, and showed that reaction is more rapid with the lower alcohols. The sequence of alcohols according to their ability to replace the chlorine atom in chlorotriazine is (increasing from left to right) — isopropanol, n-propanol, n-butanol, ethanol, and methanol.

Primary alcohols containing negative substituents, such as trifluoro-, tribromo-, and trinitroxy-methylethanol, and 2-methyl-2-nitropropanol, are also able, in the presence of an alkaline reagent, to replace the chlorine atoms in cyanuryl chloride with formation of the corresponding ethers. Substitution does not take place with nitroethanol and 2-nitrobutan-1-ol, probably because primary and secondary nitro-compounds exist in alkaline medium as *aci*-forms; these react with cyanuryl chloride at the *aci*-hydrogen atom to form an unstable ester, which cannot be isolated [122].

In several cases the presence of an alkaline reagent is insufficient for the reaction to succeed, and considerably better results are obtained by using 2,6-dialkylpyridines to combine with the acids [123], especially good results being obtained with 2,4,6-trimethylpyridine [36].

Alkali-metal alkoxides, even in equivalent proportions, usually yield with cyanuryl chloride only the triethers [117,124-126]. Cases are known in which the three chlorine atoms are substituted in the presence of an alkali metal. This occurs with cyanuryl chloride and 2,3-epoxypropanol [127] in the proportions 1 : 3 (in the presence of sodium) in anhydrous medium (for example benzene) at 0–15°, the yield of 2,4,6-trisepoxypropyltriazine being 95%. The reaction with 1-chloro-2,3-epoxypropane is similar; the mechanism of the reaction is not indicated.

In the presence of alkalis cyanuryl chloride and other chlorotriazines are able to react with cellulose. The reaction is analogous to benzoylation or acetylation, and takes place both in organic solvents [128,129] and in water [81]. In the latter case the main reaction is accompanied by hydrolysis. In aqueous medium such hydrolysis has prevented the replacement of only one chlorine atom with formation of a cellulose ether and the dichloride of cyanuric acid.



In the absence of acid-binding reagents, heating cyanuryl chloride with alcohols yields cyanuric acid and hydrogen chloride, the degree of etherification being slight. At low temperatures, however, cyanuryl chloride reacts with methanol to form the triether, reaction being more rapid than in the presence of such reagents as $NaHCO_3$ and $CaCO_3$. The difference in reaction velocity is due to the catalytic action of the hydrogen chloride evolved [130].

In contrast to alcohols, phenols react with cyanuryl chloride and other chlorinated triazines with greater difficulty. Reaction requires a fairly high temperature or the use of alkali-metal phenoxides. Thus when cyanuryl chloride (1 mole) reacts with sodium phenoxide (3 moles) in aqueous acetone at 25°, all three chlorine atoms are replaced to give a 95% yield of the triether [116]. In order to obtain the same compound from phenol, the temperature must be raised to 170–200°. [116,131]

Although the stepwise character of the reaction of cyanuryl chloride with phenols is smoothed out, owing to the weaker deactivating influence on the remaining chlorine atoms of the OAr group compared with OAlk and to the lower reactivity of phenols, it is possible by suitable choice of the reaction conditions to replace the chlorine atoms in cyanuryl chloride successively by phenoxy-groups [116,117,132]. The Cl atoms in 2-amino-4,6-dichlorotriazine can also be replaced successively by OAr [116]. When the reaction is first carried out with phenol and sodium carbonate at 65°, 2-amino-4-chloro-6-phenoxytriazine is obtained; when this is treated with sodium phenoxide at 100°, 2-amino-4,6-diphenoxytriazine is formed. The latter is obtained also when 2-amino-4,6-dichlorotriazine is treated with sodium phenoxide at 100°. 2,4-Diamino-6-phenoxytriazine can be prepared in a similar manner from the corresponding monochloro-derivative; when an amino-derivative of chlorotriazine is treated with phenol itself, substitution takes place only at 200°, the amino-group being partly replaced by the phenoxy-group [116].

The best results in stepwise substitution of the chlorine atoms are achieved in the presence of pyridine, 2,6-dimethylpyridine, 2-methylquinoline, and 2,4,6-trimethylpyridine [75].

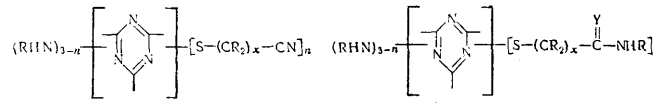
Phenols containing an aldehyde group react smoothly. Thus gradual addition of an alcoholic solution of *o*-, *m*-, or *p*-hydroxybenzaldehyde to cyanuryl chloride in acetone yields the 2,4,6-trisformylphenoxytriazine. This latter compound reacts in acid medium with 4-oxo-2-thiothiazolidine and its 3-ethyl and 3-phenyl derivatives to form the

corresponding 2,4,6-tris-(4-oxo-2-thiothiazolidin-5-ylidenemethylphenoxy)triazines, which possess strong fungicidal properties [37].

4. Reactions with Sulphur-Containing Compounds

Cyanuryl chloride and other chlorinated triazines react with thiols or their alkali-metal derivatives to form sulphides. The chlorine atoms are exchanged for alkylthio- and arylthio-groups still more readily [75] than for alkoxy- and aryloxy-groups. For example, one chlorine atom in cyanuryl chloride is exchanged at -25° to -30° by the action of methanethiol, and at 0° by the action of ethanethiol. Owing to the great activity of thiols, reaction takes place more readily with substituted chlorotriazines too [75].

Various thiol derivatives — mercapto-nitriles [133], mercapto-amides [134], and their salts — have been used in reactions with cyanuryl chloride, when compounds of types (XXIX) and (XXX) are formed depending on the conditions.



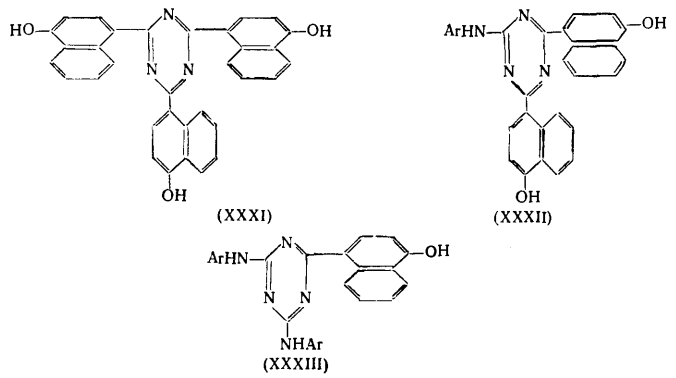
(XXIX) (XXX)

Cyanuryl chloride and other chlorinated triazines react also with the following compounds — thiocyanic acid and its salts [135], thiourea [136], 5-substituted 4-methyl-2-mercaptothiazoles [137], ethyl 2-mercaptothiazol-4-ylacetate [138], dialkyldithiocarbamates [34,139], the sodium derivative of 2-mercaptobenzothiazole [140], thioglycollic acid [141], and mercaptoalkanesulphonates [142]. The reaction products obtained from cyanuryl chloride and many of the above compounds exhibit the properties of insecticides, fungicides, and weed-killers. An especially active fungicide is 6-chlorotriazine-2,4-diyl bisdimethyldithiocarbamate, which is prepared from cyanuryl chloride and sodium dimethyldithiocarbamate [34].

Sodium hydrogen sulphide reacts similarly to thiols and their metallic derivatives with cyanuryl chloride [143], the monosodium salt of trithiocyanuric acid being formed.

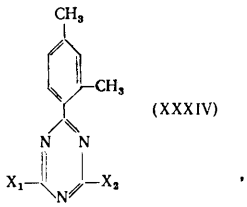
5. Reactions with Formation of a C–C Bond

Cyanuryl chloride can undergo the Friedel–Crafts, Wurtz, and Grignard reactions, with formation of aryl- and alkyl-triazines. For example, cyanuryl chloride and other chlorotriazines can be condensed with phenols [7,64], in particular with 1-naphthol to give the compounds (XXXI)–(XXXIII).



(XXXI) (XXXII) (XXXIII)

Interaction between cyanuryl chloride, benzene, and aluminium chloride has been reported [144]. However, no success was achieved [64] in obtaining a phenyl- or triphenyl-triazine derivative in this way. Later the reaction of cyanuryl chloride with benzene or its homologues in the presence of aluminium chloride and a small quantity of water (at the boiling point) has been patented in the German Federal Republic [145]; 2,4,6-triphenyltriazine and 2,4,6-tri-*o*(and *p*)-tolyltriazines have been obtained in this way. In the absence of water, without the temperature being raised, a compound of general formula



(XXXIV)

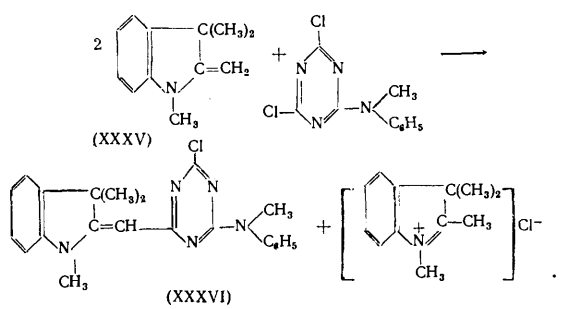
could be obtained in which X_1 represents chlorine and X_2 represents chlorine or 2,4-dimethylphenyl. The reaction is carried out in the presence of aluminium chloride and in an inert solvent; depending on the quantity of xylene, the products are 2,4-dichloro-6-(2,4-dimethylphenyl)triazine and 2-chloro-4,6-bis-(2,4-dimethylphenyl)triazine, which are intermediates for vat dyes [146].

Cyanuryl chloride undergoes the Wurtz–Fittig reaction with iodobenzene and bromophenetole, to form the corresponding triaryltriazines [147–149].

Reaction of cyanuryl chloride with a Grignard reagent can yield, depending on the reaction conditions, mono-, di-, or tri-alkyl or -aryl derivatives containing either identical or different radicals [150–153].

Carbon–carbon bonds are formed in the reaction of cyanuryl chloride with diethyl malonate. Only one chlorine atom is replaced if the ester is used in the base-catalysed reaction. With sodiomalonic ester, all three chlorine atoms can be replaced [6].

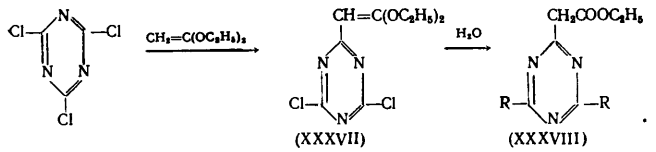
Cyanuryl chloride reacts similarly with other compounds containing an active methylene group. Thus, depending on the reaction conditions, 1,3,3-trimethyl-2-methyleneindoline (XXXV) can successively substitute the chlorine atoms to form the corresponding derivatives, for example 2,4-dichloro-6-(1,3,3-trimethylindolin-2-ylidenemethyl)triazine [154,155]. If one chlorine atom of cyanuryl chloride is first substituted by means of *N*-methylaniline, and then a second chlorine atom by means of (XXXV), the monochloro-derivative (XXXVI) is formed:



(XXXV) (XXXVI)

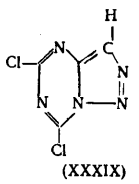
Similar behaviour to (XXXV) is shown by other heterocyclic bases containing methylene groups, for example 1,2-dihydro-1-methyl-2-methylenequinoline, 2,3-dihydro-3-methyl-2-methylenebenzothiazole, and also 1,1-bis-*p*-dimethylaminophenylethylene [156].

1,1-Diethoxyethylene also reacts at the methylene group with cyanuryl chloride[157]. The product (XXXVII) hydrolyses to the esters (XXXVIII), those in which R represents Cl or OH being formed in greater or smaller amounts depending on the conditions:



(XXXVII) (XXXVIII)

Cyanuryl chloride reacts with diazomethane[158], when only one chlorine atom is usually replaced by the *α*-diazoalkyl group; a second chlorine atom is replaced with difficulty. The reaction is carried out with excess of diazomethane, which also acts as a neutralising agent, being decomposed by hydrochloric acid into methyl chloride and nitrogen. The product is given the structure

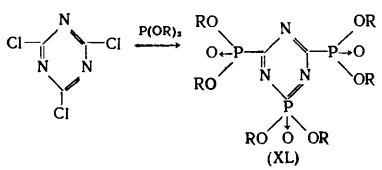


(XXXIX)

Reduction of 4,6-disubstituted 2-diazomethyltriazines with hydrogen sulphide or a thiol yields the corresponding 4,6-disubstituted triazine-2-aldehyde hydrazones, which can be converted into the free aldehydes. When 2,4-dichloro-6-diazomethyltriazine is reduced with ethanethiol in the presence of alkali, 4,6-dimercaptotriazin-2-al hydrazone is first formed, and then the corresponding aldehyde[159].

6. Various Substitution Reactions

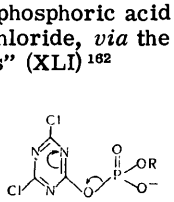
The reaction of cyanuryl chloride with trialkyl phosphites is analogous to the Arbuzov reaction for alkyl halides and results in the formation of alkylphosphonic esters. The three chlorine atoms are readily substituted, with the formation of triesters of triazinetriphosphonic acid (XL)[160]



(XL)

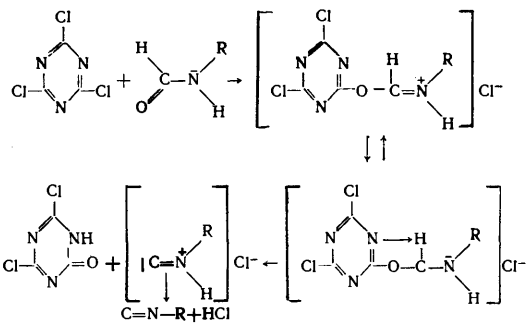
Other organophosphorus compounds derived from cyanuryl chloride have been obtained[161].

Various diesters of phosphoric acid can also be obtained by means of cyanuryl chloride, *via* the intermediate formation of "enol phosphates" (XLI)[162]



(XLI)

With sodium azide cyanuryl chloride forms the dangerously explosive cyanuryl triazide[6]. With monosubstituted formamides it forms the corresponding isocyanides, the reaction being represented by the scheme[163]



The action of hydrogen halides on chlorinated triazines results in halogen exchange. Thus reaction of 57% hydriodic acid with cyanuryl chloride in the cold yields a mixture of 2,4,6-triiodo- and 2-chloro-4,6-diiodotriazines[6]. Elimination of methoxyl from 2,4-dichloro-6-*o*-methoxyphenyltriazine with hydrogen bromide is accompanied by replacement of chlorine by bromine. In order to obtain 2,4-dichloro-6-*o*-hydroxyphenyltriazine, therefore, the bromine must subsequently be displaced by chlorine by the vigorous action of hydrogen chloride[82,164].

Replacement of the chlorine by fluorine atoms was at first accomplished by treating cyanuryl chloride with hydrogen fluoride[165], and later with potassium fluorosulphate[166]. In the latter case partial substitution products are formed as well[167]. Triazine fluorides have also been obtained by treating the corresponding chloro-derivatives with the Swarts reagent (a mixture of about 10 moles of antimony trifluoride, 1 mole of antimony trichloride, and 3 moles of chlorine[168]). The triazine fluorides are very toxic.

7. Reduction of Cyanuryl Chloride and Other Chlorinated Triazines

Cyanuryl chloride is unaffected by most strong reducing agents. It is not reduced by hydrogen iodide. On treatment with lithium tetrahydroaluminate in ether at -10°, 2,4-dichlorotriazine is obtained[169,170]. 2,4-Dichloro-6-dimethylaminotriazine is also formed owing to reductive cleavage of the triazine ring in the initially formed dichlorotriazine, and subsequent reaction of the resulting dimethylamine with unchanged cyanuryl chloride.

Under ordinary conditions reaction of cyanuryl chloride with lithium tetrahydroaluminate in ether yielded only inorganic reaction products, formed by decomposition of the initially produced triazine under the influence of aluminium chloride, which is also a product of the reaction[6].

Other chlorotriazines can be reduced to the corresponding substituted triazines. Thus 2-amino-4,6-dichlorotriazine and 2,4-diamino-6-chlorotriazine are reduced by hydrogen iodide in the presence of phosphorus to 2-amino- and 2,4-diamino-triazines[171]. 2-Amino-, 2-alkylamino-, and 2-phenoxy-triazines have been obtained by hydrogenating the corresponding chloro-derivatives in the presence of a palladium–carbon catalyst[151]; 2,4-dimethoxytriazine has been prepared in a similar manner[172].

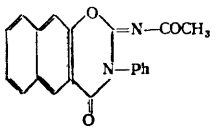
Sometimes, however, direct replacement of chlorine by hydrogen does not go well owing to poisoning of the catalyst. In these cases an indirect method of reduction is employed:

chlorine is first replaced by a methylthio-group, and the resulting derivative is then reduced in the presence of Raney nickel[173,174].

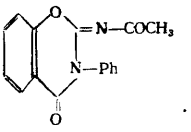
8. Reactions with Transformation of the Ring

Several of the substitution reactions of cyanuryl chloride take place under fairly severe conditions, but rupture of the triazine ring is not observed. Ring cleavage accompanying reduction of cyanuryl chloride with lithium tetrahydroaluminate is due to the intermediate formation of triazine. The cyclic system of cyanuryl chloride breaks down only on treatment with concentrated sulphuric acid at 150°.[64]

Reactions involving breakdown of the ring are known with several triazine derivatives which are obtained from cyanuyrl chloride. Thus when the products from the reaction of cyanuryl chloride with anilides of 3-hydroxy-2-naphthoic and salicylic acids are boiled with acetic anhydride in the presence of a few drops of pyridine, substances are formed which can be proved to have the structures (XLII) and (XLIII)[175]. These could result only from opening of the triazine ring.

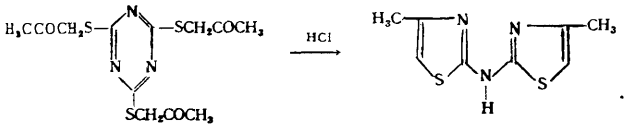


(XLII)

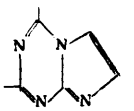


(XLIII)

Other triazine derivatives also show ring cleavage. For example, 2,4,6-triacetonylthiotriazine on treatment with hydrochloric acid undergoes the following reaction[176]



From 2,4-dichloro-6-hydroxyethylaminotriazine have been obtained, by a series of reactions, 2,4-disubstituted 6,7-dihydroimidazo[1,2-*a*]triazines[177]. Although this does not involve opening of the ring, the "aromatic" triazine system is disrupted by reaction at a cyclic double bond with formation of the bicyclic system



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SELF-DIFFUSION AND INTERDIFFUSION IN POLYMER SYSTEMS

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I. INTRODUCTION

During the past two decades the diffusion of substances of low molecular weight in high polymers has formed the subject of numerous researches by both Soviet and foreign investigators, among whom must be mentioned Reitlinger, Zhurkov, Ryskin, Malinskii, and Vasenin in the Soviet Union, and Barrer, Crank, Long, Park, Auerbach, Van Amerongen, McCall, Stamm, and many other workers abroad. In contrast, the phenomena of self-diffusion in polymers and of the diffusion of one polymer into another (interdiffusion) have remained little investigated because of the great experimental difficulties and the complexity of the theoretical interpretation. Nevertheless, these phenomena are of great scientific interest and immense practical importance. As we shall see below, very many properties of polymers are to some extent linked with the ability of flexible macromolecules or their segments to diffuse. The capacity for self-diffusion and interdiffusion of polymers is no less important for their processing and application.

The purpose of the present review is to summarise results on the self-diffusion and interdiffusion of polymers having flexible molecules (elastomers) and to outline directions for future research on this problem.

II. METHODS FOR THE EXPERIMENTAL INVESTIGATION OF SELF-DIFFUSION AND INTERDIFFUSION IN POLYMER SYSTEMS

The first experimental investigations of self-diffusion were based on a study of the self-adhesion of polymers, which several workers have shown [1-5] to depend on the interpenetration and intertwining of flexible macromolecules under the influence of thermal motion. The method consisted in placing two specimens of the same polymer in

contact with one another for a definite time, and determining the resistance which must be overcome to separate them[6,7]. From the dependence of self-adhesion on temperature this method enables the apparent activation energy of the process to be calculated by means of an equation analogous to the Arrhenius equation, on the assumption that the strength of the bond produced by self-adhesion is a measure of the diffusibility of the polymer.

On the basis of the results obtained for self-adhesion, several qualitative hypotheses were made, at the very beginning of the past decade, concerning the mechanism of the self-diffusion and interdiffusion of polymers, as well as the dependence of these processes on particular characteristics of the polymer, such as molecular weight, the proportion of three-dimensional structures, the degree of branching of the macromolecules, and the presence of polar groups in the latter. The method used also enables the exponential temperature dependence of the self-diffusion (self-adhesion) of polymers to be established. Such a dependence is characteristic also of the diffusion of substances of low molecular weight[8].

In 1952 Bueche *et al.*[9] first reported measurements of the self-diffusion of polymers by a tracer method. Plasticised polystyrene prepared from styrene labelled with the ^{14}C isotope at the second atom in the side-chain and a copolymer prepared from 99% of n-butyl acrylate and 1% of labelled styrene were used. Measurements of diffusion were made by the method of Rayner *et al.*[10], in which a thin layer of the radioactive substance is deposited on a flat block of the same substance possessing no radioactivity. As the radioactive substance diffuses into the non-radioactive, the β-ray intensity, measured on a counter placed over the specimen, decreases through absorption of the rays by the material of the block. Thus the rate of diffusion can be assessed from the decrease in intensity of the radiation.

The above work showed that the coefficients of self-diffusion, which lay within the range 10^{-11}–10^{-12} cm^2 s^{-1}, were roughly inversely proportional to the viscosity of the polymer. The activation energy of self-diffusion calculated from these results for the n-butyl acrylate–styrene copolymer was 13.2 kcal mole^{-1}, the activation energy for viscous flow of the same copolymer being 13.8 kcal mole^{-1}. Similar results were obtained in other cases: the activation energies of self-diffusion and viscosity were the same within the limits of experimental error. Since in the opinion of Bueche *et al.* a comparatively simple relation exists between the coefficient of self-diffusion and the viscosity, and since it is far easier to measure the latter than self-diffusion, Bueche considers[11] that this relation provides a simpler method for assessing molecular motion in a solid polymer.

Quite recently Bresler *et al.*[12] have also investigated the diffusion of polymers by means of labelled atoms. By an analogous method to the above[10] they have examined the diffusion of macromolecules of tritium-labelled synthetic polyisoprene into natural rubber.

The temperature of the specimen in the diffusion measurements could be adjusted between 22° and 140°. The coefficient of diffusion into natural rubber of synthetic polyisoprene having molecular weights within the range 8×10^3–2.8×10^4 lies between 6×10^{-13} and 0.9×10^{-13} cm^2 s^{-1} at 100°. In the case of the polyisoprene fraction of molecular weight 1.1×10^4, the coefficient of diffusion into vulcanised natural rubber at 100° was determined, and found to be about 1.4×10^{-13} cm^2 s^{-1}. These values are seen to be considerably lower than those reported in Ref. 9. Nevertheless, the activation energy for macromolecules of molecular weight 11 000 was, according to the results of Bresler *et al.*, 8.7 kcal mole^{-1}, which is just as low as in the case of substances of low molecular weight diffusing into unvulcanised rubber.

From the low activation energies found, quite unrelated to the large molecular volume of the diffusing polymer molecules, Bresler and his coworkers concluded that only a small portion of the polymer chain — probably one or a few monomer units — takes part in each elementary act of diffusion.

In the opinion of these workers[12], the comparatively slight variation in diffusion coefficient found to occur with change in the molecular weight of the diffusing species indicates that the polymer chains are not entangled, at least up to a molecular weight of 30 000. According to Bresler, this supports the bundle hypothesis of polymer structure developed by Kargin *et al.*[13,14] The observed lower coefficient of diffusion into vulcanised rubber has been explained by the formation of a three-dimensional network in the polymer on vulcanisation, which represents additional resistance to diffusion.

The interdiffusion of different kinds of polymers has been investigated by Krotova and Morozova. In their first paper[15] they had examined under the microscope sections through two-layer films of the polymers. On contact between two non-polar polymers, for example polyethylene and polyisobutylene, the interface was found to be diffuse, from which it was concluded that in this case the establishment of an adhesive bond is due to interdiffusion in the contact zone.

In later work Krotova and Morozova[16] used microscopic observation under ultraviolet radiation to study the boundary between fluorescent polymers. They found that the interface was very blurred in systems formed by non-polar polymers of similar structure. Heat-treatment of duplex films produced a sharp increase in the diffuseness of the boundary. Systems in which the components differed greatly in chemical structure (polar and non-polar) gave a narrow zone of blurring (of 1 μm and less). In contrast to the first paper, the second paper by Krotova and Morozova expresses the view that the blurring of the boundaries is due, not to the diffusion of macromolecules or their segments, but to the transfer of entire structural components from one phase to the other.

From all that has been said above, it is readily seen that investigation of the self-diffusion and interdiffusion of polymers is just beginning. The results obtained can be regarded only as crudely tentative, and a great deal of work remains to be done before the corresponding coefficients can be determined with sufficient accuracy. However, the actual fact of the diffusion of sufficiently flexible molecules, or at least of segments thereof, in the bulk of the polymer, is obviously no longer open to doubt at the present time.

Among the methods available for studying diffusion phenomena in polymers, radiometric methods seem to us especially promising. At one time such methods enabled self-diffusion to be examined in metals[17], and they are now widely employed to study the diffusion of substances of low molecular weight into polymers[18,19]. Methods based on microscopic observation of the interpenetration of polymers, in either ordinary light or ultraviolet radiation, are less suitable owing to their relatively low sensitivity. However, examination of cross-sections of duplex polymer

films under the electron microscope can undoubtedly give extremely interesting information, since in this case a resolution of 15–20 Å may be achieved. The extremely thin sections required for observation of the self-diffusion and interdiffusion of polymers are now readily obtainable with ultramicrotomes.

Infrared spectroscopy could also be used to investigate the interdiffusion of polymers. When two thin transparent films of polymers containing different characteristic groups capable of energetic interaction are brought into contact, the absorption spectrum should change as diffusion proceeds, involving both the appearance of new bands corresponding to such interaction and weakening of the old bands. This could serve as evidence of the penetration by diffusion of one polymer into the other.

Finally, nuclear magnetic resonance may be expected to provide a very useful method for studying the self-diffusion and interdiffusion of polymers. Much work has recently been done on the application of this method to the study of polymers, among which must be mentioned that of Slichter, Sauer, Wall, Woodward, McCall, and several other investigators. These workers have provided valuable information on the motion of polymer segments and on the influence of various factors on this motion. Some of their results will be discussed below.

The self-diffusion and interdiffusion of polymers are sharply distinguished by one feature from the diffusion of substances of low molecular weight into a polymer; whereas a small molecule can diffuse into a substrate completely independently of other molecules of the same substance, this is not the case with the diffusion of polymer segments, since the macromolecules can intertwine with one another, become entangled, and form loops. As a result of the stresses arising in the chains, the diffusing segments may sooner or later cease their forward movement, and the process may come to a halt. The presence of crystallites or other structural elements, for example bundles, may provide a similar obstacle to the further progress of diffusion phenomena. Several papers[20] refer to the significance of the interlacing of molecules in the viscous flow of polymers. However, such flow is caused by the application of an external stress gradient, which tends to orient, straighten out, and hence disentangle the chains[21]. This does not, of course, apply to diffusion.

Thus it may be supposed that the rate of diffusion, represented by the advance of the front formed by the ends of the diffusing polymer molecules, will not be constant, but will gradually decrease with time, and the equilibrium state of the system, corresponding to maximum entropy, will in practice never be reached. This may be the reason for the low values which have been obtained[9,12] for the coefficient of self-diffusion. For the same reason, only methods which enable the interpenetration of molecules to be measured within very short distances (electron-microscopy, radiometry) are suitable for determining the diffusion coefficient of segments of macromolecules.

III. MECHANISM OF SELF-DIFFUSION AND INTERDIFFUSION OF POLYMERS

Present-day views on the mechanism of viscous flow and diffusion in liquids are based on the so-called "hole" theory of liquids put forward by Frenkel'[22–24] and independently by Eyring[25]. Their views on viscous flow and diffusion in liquids of low molecular weight are now widely known[26,27], and we shall not discuss them further. The mechanism of the diffusion of macromolecules in liquids of low molecular weight, and especially the mechanism of self-diffusion and interdiffusion in incompletely vitrified amorphous polymers, the flexible molecules of which are capable of thermal motion, are far less clear and have been far less studied. Nevertheless, it is already possible, on the basis of general considerations, analogies with diffusion in systems formed by simple molecules, and certain experimental results, to visualise roughly the molecular pattern of self-diffusion and interdiffusion in polymers.

In amorphous polymers having flexible molecules, just as in liquids of low molecular weight, short-range order is present but long-range order absent. As in ordinary liquids, holes or microvoids occur in such systems. However, these microvoids are not large enough to contain an entire molecule. Furthermore, in a high polymer the position of each monomer unit is determined not only by interaction with units in neighbouring molecules but also by adjacent and more remote units in the same chain. Therefore the simultaneous displacement of the whole macromolecule to a new position is impossible: it would require too high an activation energy.

With sufficiently flexible macromolecules, however, individual segments may move, forming in this case the kinetic units. As a result, any segment of the molecular chain which is close to a microvoid can be displaced without producing a change in the arrangement of the other parts of the macromolecule. Such movement obviously does not require too great energy to overcome the activation barrier. Thus the elementary process in the self-diffusion or interdiffusion of elastomers is an intermittent transition to a fresh equilibrium position, not of the whole macromolecule but only of a segment thereof, comprising a comparatively small number of carbon atoms. The activation energy for displacement of a molecule approaches asymptotically a definite value as the number of carbon atoms in the linear molecule increases to 25–30. Moreover, it has been shown by an extrapolation method that the activation energy of viscous flow in linear hydrocarbons of high molecular weight is equal to the activation energy required for the viscous flow of segments consisting of about 20 carbon atoms[28,29]. On this basis Eyring considers that, for sufficiently long chains, the mean size of a segment which can move in the above way is a chain length comprising 20–30 atoms. Flory reached similar conclusions[30].

The size of segment representing the kinetic unit is not, of course, constant, being determined primarily by the flexibility of the molecular chain, the intensity of molecular interaction, and the temperature. It is also obvious that segments of different sizes can take part in self-diffusion and interdiffusion.

The movement of segments of a macromolecule always produces some change in conformation of a chain molecule. As a result, a large number of successive movements of segments will lead not only to a change in shape of the macromolecule (Kuhn's micro-Brownian motion) but also to a shift in its centre of gravity, *i.e.* to a "wandering" of the macromolecule in the mass of polymer (macro-Brownian motion). Of course, owing to the very high viscosity of the system, movement of the whole molecule in the mass of polymer will be extremely slow, and in some cases, when sufficiently strong intermolecular bonds are formed, may be completely absent.

In the absence of external forces, the micro-Brownian and macro-Brownian motion of a polymer chain molecule is completely random, in any direction. The action of external forces, for example a shear stress, affects both types of motion. Macro-Brownian motion will then take place irreversibly, and a process of flow will start. Micro-Brownian motion, if unaccompanied by relative movement of whole molecules, will produce orientation of the molecules in the direction of the force. After the force has ceased to act, however, the molecules will again adopt the thermodynamically most probable conformations as a result of the action of conformational (entropy) elasticity caused by the micro-Brownian motion.

The effect of temperature on the self-diffusion and interdiffusion of polymers is similar to that on the diffusion of simple liquids. With rise in temperature, thermal expansion of the polymer results in the appearance of further microvoids with an increased probability of activation of segments lying close to holes. As a result, the segments will overcome more easily the energy barrier to movement into a microvoid, and diffusion will be more rapid[31].

Brandt[32] has recently put forward the hypothesis that the elementary act of diffusion in polymers consists in two activated polymer chains parting to allow a small molecule (or segment of a macromolecule) to pass through. He considers that the activation energy of diffusion in polymers is made up of an intermolecular component E_i due to mutual repulsion between molecules and their neighbours (*i.e.* internal pressure) and an intramolecular component E_b due to the forces tending to inhibit internal rotation in the macromolecules.

As the temperature is raised, increasing numbers of segments of an individual macromolecule will obviously take part in diffusion phenomena, with an ever increasing kinetic energy. Finally, a point is reached, at a definite temperature, at which the sum of the activation energies for the individual segments exceeds the energy barrier for the whole macromolecule, which will make it possible for the latter to take part in diffusion as a whole. This can obviously take place only if this temperature is below that at which the polymer decomposes.

Quite recently Vasenin[33] has attempted a quantitative approach to the self-diffusion of polymers. On the assumptions that only the terminal portions of molecules are capable of diffusion and that short branches impede diffusion, while sufficiently long branches can themselves act as free ends, he derived an equation linking the strength of the self-adhesion bond with such factors as rate of separation, time of contact, molecular weight of polymer, etc. A test of this equation was satisfactory to a first approximation: graphs of the variation in strength of self-adhesion with time of contact and with molecular weight of the polymer were similar in shape to the corresponding experimental curves[4,6,7], although calculated absolute values of the adhesive strength were greater than the experimental values. The theory also provides a good explanation of the increase in self-adhesion strength with increase in the number of sufficiently long branches, with rise in the contact temperature, and with increase in the polydispersity of the polymer.

Vasenin's theory is still far from perfect. In particular, it is doubtful whether the molecules can diffuse only at their ends. As Vasenin himself points out, it is probable that under certain conditions the middle portions of the chains can diffuse. Further, it seems to us that the theory has not taken into account the effect on diffusion of entanglement of the chains, which has already been discussed above. It is perhaps for this reason that the calculated values of the self-adhesion strength were greater than the experimental values. Finally, the physical significance of some of the coefficients in Vasenin's equation is not entirely clear. Nevertheless, this work is undoubtedly of interest as the first quantitative treatment of self-adhesion, and hence of self-diffusion.

In conclusion it must be stated that the above molecular picture of self-diffusion and interdiffusion is only a crude approximation to the process which actually occurs. At the present time the concept of the bundle structure of polymers[13,14] is becoming more and more widespread. The presence of bundles and other structural elements of higher order (ribbons, lobes, globules) in real polymers must undoubtedly affect self-diffusion and interdiffusion, complicating the elementary act and giving to these processes their characteristic features. Obviously the quantitative theories of these phenomena, too, must be corrected for the presence of supermolecular structures in high polymers.

IV. INFLUENCE OF TIME, TEMPERATURE, AND CONCENTRATION ON SELF-DIFFUSION AND INTERDIFFUSION IN POLYMERS

As already mentioned, very little direct research has yet been done on diffusion and interdiffusion in polymer systems. In writing the present section and the next, therefore, we have made extensive use of the well-known relation between self-diffusion (interdiffusion) and self-adhesion (adhesion) of polymers. Furthermore, in considering the effect of various factors on diffusion phenomena in elastomers, we have been forced to turn, owing to the inadequacy of the experimental data, to analogies between the diffusion and interdiffusion of polymers, on the one hand, and the diffusion into polymers of substances of low molecular weight on the other.

Effect of Time

The variation of the self-diffusion of polymers with time can be assessed from results[6,7], obtained by the separation method, on the dependence of the self-adhesion of polyisobutylenes of different molecular weights on the period of contact. As a result of the interpenetration of molecular chains by diffusion, the self-adhesive strength increased in all cases with time, at first rapidly and then more and more slowly, tending to a definite limit. The increase in self-adhesion strength with time, and hence also the increase in the rate of diffusion, were greater the shorter the molecule. These results indicate that, in the case of polymers, diffusion takes place mainly at the ends of the molecular chains. Other investigators have expressed[34-38] a similar view, most of them considering that during diffusion a linear macromolecule is oriented parallel to the direction of diffusion.

Forbes and McLeod[4] determined the self-adhesion strength from the resistance to rupture of specimens of the same high polymer which had been brought into contact. They found that the period of contact necessary for the self-adhesion strength to become equal to the cohesive strength varied within very narrow limits for different polymers.

Thus this time was only 3–5 min for butyl rubber, while it was 4–5 h for natural rubber and 14–17 h for a butadiene–styrene copolymer. It is significant that in these experiments the limiting self-adhesion strength, equal to the cohesive strength, was reached with all the polymers investigated which had rubberlike elasticity at ordinary temperatures. The situation is different with rigid thermoplastics, which exhibit self-adhesion only at elevated temperatures, as we shall see below.

Insufficient experimental data are available to judge whether or not self-diffusion and interdiffusion of polymers obey Fick's law. In systems comprising a substance of low molecular weight and a polymer at temperatures below the glass point of the latter, the diffusion coefficient usually varies with time[39–41]. Such variation is due either to a change in the properties of the polymer during diffusion, to conformational changes in the polymer molecules with time, or to dissolution of the crystalline regions. However, these considerations do not apply to self-diffusion or interdiffusion, since both these phenomena occur only with polymers which are not in a state of rubberlike elasticity. Another possible cause of the variation with time of the coefficient of self-diffusion and interdiffusion is the stress arising in the diffusing chains owing to their getting entangled or caught up in one another. However, this question requires special investigation.

Effect of Temperature

The temperature dependence of the self-diffusion and interdiffusion of polymers is clear from work on the influence of the contact temperature on the self-adhesion and the adhesion of polymers[6,7,42]. The temperature dependence of the coefficient of self-diffusion has been studied directly[12]. Experiments showed that self-diffusion and interdiffusion increase exponentially with rise in temperature. A similar relation has been found for the diffusion of organic molecules into polymers[19,38,43,44].

The activation energy for the diffusion of organic compounds of comparatively low molecular weight into polymers has been found in several cases[19,38,43] to increase with rise in molecular weight. This is because transition of small molecules from one equilibrium position to another in the course of diffusion requires a greater consumption of energy the larger the molecule. However, study of the temperature dependence of the self-diffusion and interdiffusion of polymers of quite high molecular weight has shown that the activation energy is practically independent of the size of the macromolecule. This confirms that the kinetic unit in the diffusion of chain molecules is not the whole molecule but only a segment thereof.

The increase in the self-adhesion of high polymers with temperature[6,7,42] occurs, of course, only over a certain range of temperatures, between the glass point and the transition point for the state of viscous flow. Below the glass point self-diffusion is impossible, so that self-adhesion is also absent. At temperatures corresponding to viscous flow of the polymer, the self-adhesion strength for a given period of contact is practically independent of temperature, since under such conditions complete coalescence of the polymer surfaces takes place almost instantaneously, and the structure characteristic of the bulk of the polymer is very rapidly established in the zone of contact. A similar situation has been observed in the welding of rigid thermoplastics[45–47].

Similar arguments can be developed for the adhesion of two polymers.

Effect of Concentration

No experimental data are available on the effect of the concentration of polymers on their interdiffusion, and discussion of this question can be based only on general considerations and analogies with the effect of concentration on the diffusion of substances of low molecular weight[48].

In the ideal case the diffusion coefficient is independent of the concentration of the substance which is diffusing. However, its value will be affected by any interaction between the diffusing molecules, an example being provided by the diffusion of water in polyethylene[49]. On reaching a definite concentration, the water molecules which have penetrated the polyethylene begin to form aggregates by hydrogen-bonding which, of course, tends to diminish their mobility and the diffusion coefficient.

On the other hand, simple molecules diffusing into a polymer can rupture the bonds between macromolecules[50,51], resulting in a change (loosening) of the structure of the system into which diffusion is taking place. It is clear that the higher the concentration of substance which has diffused, the greater will be this change, and the more sharply will the diffusion coefficient increase.

Both processes can obviously take place in the interdiffusion of polymers. The resultant effect should ultimately be determined by the relation between the energies of interaction of the diffusing molecules with one another and with the polymer molecules among which diffusion occurs. In this case, of course, the phenomenon may be complicated considerably by purely steric factors, which may be especially significant in the diffusion of polymer into polymer.

V. INFLUENCE OF MOLECULAR STRUCTURE AND PROPERTIES ON SELF-DIFFUSION AND INTERDIFFUSION IN POLYMERS

Effect of Size of Molecules

The relation between the diffusion coefficient of simple molecules moving in a polymer and their molecular weight has been studied by several investigators[19,38,45,52]. According to Auerbach *et al.*[19] the relation between diffusion coefficient D and molecular weight M can be represented by the power function

$$D = KM^{-\gamma}, \quad (1)$$

where K and γ are constants.

However, a far more definite relation was found to exist between the diffusion coefficient and the molecular volume v of the diffusing substance[43,53–55], the former decreasing with increase in the latter, not as a power function, as might be expected from the approximate proportionality of molecular volume to molecular weight, but exponentially:

$$D = Ae^{-\rho v}, \quad (2)$$

A and ρ also being constants. The exponential relation between D and v showed that the volume of a molecule has a greater influence on its rate of diffusion in polymers than has its weight.

In the case of the self-diffusion and interdiffusion of polymers, special interest attaches to the relation between diffusion coefficient and molecular length. This relation has been investigated experimentally in the case of the diffusion of alkanes into polymers by Prager *et al.*[56,57], Aitken and Barrer[37], and McCall *et al.*[58] As was to be expected, increase in the length of the molecule was found to be accompanied by a decrease in the diffusion coefficient, which was especially marked at the beginning of a homologous series.

Vasenin[59] gives the following explanation of the variation of the diffusion coefficient for alkanes into a polymer with the molecular size of the former, on the assumptions that the diffusing molecules are oriented in the direction of their motion and that the drag arising in this case can be calculated in a similar manner to that between two moving layers of a liquid[27]. If in an unbranched alkane molecule consisting of n identical CH_2 or CH_3 groups the mass of each group is m, the speed of the molecule being v, the momentum of an individual group will be mv. As a result of interaction with the relatively immobile macromolecules, each group causes an analogous group in a polymer macromolecule to move with velocity v'. From the law of the conservation of momentum, $mv = 2mv'$, whence $v' = \frac{1}{2}v$. Thus in unit time each group will transmit momentum $\frac{1}{2}mv\nu$, where ν is the frequency of collision between each group and surrounding groups of the macromolecules. The momentum transferred in unit time by all the groups is

$$F = \frac{mv}{2} \nu n. \qquad (3)$$

If this value of F, which represents the drag, is substituted in the well-known Einstein equation, with $\nu = 10^{13}$ s^{-1}, $T = 300$°K, and $m = 16$, the diffusion coefficient is found to be 3×10^{-4} cm^2 s^{-1}. This is an order of magnitude greater than the diffusion coefficient of ordinary liquids. Vasenin explains this discrepancy by the fact that the calculation took account only of the resistance due to friction at the "lateral" surface of the moving molecule, *i.e.* "lateral" or viscous resistance. In order that the molecule can move in the polymer, however, work must be done also in continually separating the macromolecular chains. The magnitude of such work will depend on the size of the gap, which will in turn be determined by the dimensions of the diffusing molecule. Thus according to Vasenin, account must be taken in diffusion not only of viscous drag but also of "frontal" resistance to movement of the molecule.

Vasenin assumes that to a first approximation the resistance to movement of a molecule in a polymer is

$$F = A\frac{mv}{2} \nu S^{\alpha} n, \qquad (4)$$

where S is the cross-sectional area of the leading group in the diffusing molecule, and A and α are constants. Substitution in the Einstein equation of the values found for F gives a relation between diffusion coefficient, S, and n

$$D = \frac{2kT}{Am\nu S^{\alpha} n}. \qquad (5)$$

In much of the work on the diffusion of simple molecules into polymers, the dependence of the diffusion coefficient on the molecular weight of the polymer has also been investigated[19,36,60-64]. The rate of diffusion of gases and substances of low molecular weight, and also the corresponding activation energy of the process, are found to be practically independent of the molecular weight of the polymer. This can be explained by the fact that the microvoids in the polymer, into which the diffusing molecules penetrate, are formed by thermal fluctuations of segments of the macromolecules, the size of which is the same over the range of molecular weights chosen.

The relation between the coefficient of self-diffusion of polymers and their molecular weights was first investigated by Bueche *et al.*[9], who used a radiometric method. In subsequent work Bueche provided a theoretical basis for the experimental relationship. Since Flory[65] had shown that the viscosity of a polymer should fall with decrease in molecular weight, it could be concluded from the experimental results that the rate of diffusion should be greater with polymers of lower molecular weight. As we have seen above, Bresler *et al.*[12] also reached similar conclusions in the case of the diffusion of synthetic polyisoprene into natural rubber at 100°. For this pair of polymers the relation between diffusion coefficient D and molecular weight M of the diffusing species can be expressed by the empirical equation $D = 6.6 \times 10^{-8} M^{-1.31}$.

The dependence of the rate of self-diffusion and interdiffusion on the dimensions of the macromolecules has been investigated indirectly also by Voyutskii *et al.*[7,66,67] in experiments on the self-adhesion and adhesion of polymers. Work with polyisobutylenes of different molecular weights showed[7] that the increase in the self-adhesion strength with time, due to the interpenetration of molecules as a result of diffusion, is greater the lower the molecular weight. In a similar manner it has been shown[66,67] that the rate and depth of diffusion of macromolecule segments of butadiene–acrylonitrile rubbers into a polyamide are greater the lower the molecular weight of the diffusing molecules. An analogous relation between self-diffusion and molecular weight has been observed by Forbes and McLeod in an investigation of the self-adhesion of polyisoprenes of different molecular weight[4].

According to Bueche[11] the presence of free ends of polymer chains results in a loosening of the polymer, thus favouring the occurrence of diffusion processes therein.

The dependence of the diffusion coefficient of high polymers on their molecular weight is certainly also affected by the fact that movement of a macromolecular chain inside a polymer is retarded not only by friction with neighbouring macromolecules but also by segments of the latter getting caught on a diffusing macromolecule. The number of points at which this occurs will be greater the higher the molecular weight. Bueche has made a detailed examination[20] of the role of such attachments in the displacement of molecules in polymers.

Let us now consider briefly the data available on the dependence of the activation energy of diffusion E in polymers on the size of the diffusing molecules. Since E is proportional to the energy required to form a microvoid into which the diffusing molecule or a segment thereof can move, it should be greater the larger the kinetic unit. This has in fact been shown by Van Amerongen[68] and by Mears[69] for diffusion of gas molecules in polymers, the latter obtaining a linear relation between E and the square of the diameter of the molecules.

In the diffusion of alkane molecules into polymers, however, E does not increase indefinitely with increase in chain length, but approaches asymptotically a constant limit[55,70]. This led Kokes and Long to assume that, in the diffusion of alkanes in polymers of the same nature, each elementary act results in displacement of the molecule by the same amount, independently of its length.

The dependence of the apparent activation energy of the self-diffusion of polymers on their molecular weight was first investigated by Voyutskii *et al.*[6,7] in experiments on the temperature variation of the self-adhesion of polyisobutylenes differing in molecular weight. In this case the activation energy was found not to be a function of the molecular weight of the polymer. This was attributed to the uniform size, independent of the length of the molecular chain over the range of molecular weights selected, of the kinetic units taking part in self-diffusion. Later Bresler *et al.*[12] also concluded that the activation energy of diffusion is independent of the molecular weight of the polymer.

Effect of Shape of Molecule

The rate of movement of macromolecules in a polymer is very greatly influenced not only by the length of the diffusing molecules but also by their degree of branching. Aitken and Barrer[37] remark that the introduction of methyl side-groups into a molecule decreases the diffusion coefficient far more than does introduction of the same group into the main chain. According to these workers, the coefficient of diffusion into rubber for butanes and pentanes of different structures decreases in the sequence:

$$n\text{-}C_4H_{10} > n\text{-}C_5H_{12} > iso\text{-}C_4H_{10} > iso\text{-}C_5H_{12} > neo\text{-}C_5H_{12}.$$

Aitken and Barrer found a linear relation between the diffusion coefficient and the product of the minimum dimensions of the diffusing molecule. Park[54] reached similar conclusions from the relation between the diffusion coefficient and the size of the minimum orifice through which a molecule can move.

Vasenin[59] explains the diminished diffusion coefficient in the presence of side-groups by the work which must, of course, be done to increase the size of the microvoid into which the diffusing molecule moves. This work should obviously be proportional to the increase in cross-sectional area of the molecule resulting from the presence of the side-group. Using the above relations for the variation of the diffusion coefficient with the cross-sectional area of the molecule S and the number of group units n, Vasenin obtained the following equation linking the diffusion coefficient D of a given molecule with the diffusion coefficient D_1 of the first member of the homologous series

$$D = \frac{D_1}{\sigma^{\alpha n}}, \qquad (6)$$

where $\sigma = S/S_1$ is the relative increase in cross-sectional area of the molecule due to the presence of the side-group.

An approximate value can be obtained for the relative cross-sectional area of hydrocarbon molecules by determining the linear dimensions of normal and isomeric alkanes[37]. On multiplying the minimum dimensions of isoalkane molecules and of the methane molecule, and dividing the first product by the second, we readily find that for neopentane $\sigma = 2.1$, while for isoalkanes $\sigma = 1.75$. Vasenin compared experimental values obtained by other workers for diffusion coefficients into various polymers with values calculated from the above formula. Although in some cases the difference between calculated and experimental values reaches 30%, this test of the applicability of Vasenin's proposed equation must be regarded as satisfactory. The observed discrepancy between calculated and experimental diffusion coefficients is due to the fact that the latter were taken from different papers and had been determined by different methods. Furthermore, the error involved in determining diffusion coefficients is at best about 10–15%.

The diffusion coefficient is affected by the presence of side-groups not only in the diffusing molecules but also in the chains of the polymer into which these molecules diffuse. In this case, however, the effect of the side-groups on diffusion is usually precisely the opposite, since such groups tend to weaken interaction between molecular chains and result in a less dense packing of the macromolecules in the polymer. The presence of long branches in the macromolecule should have a similar effect on diffusion.

Papers on the dependence of self-adhesion and adhesion in polymers on their structure contain many data on the influence of side-groups and branches in the molecular chains on self-diffusion and interdiffusion.

Voyutskii and Vakula[71] have shown, on the basis of a large number of experimental results, that the adhesion of polymers, due to interdiffusion of the molecules, always falls with increase in the number of side-groups in the molecular chains. Furthermore, adhesion always decreases with increase in volume of the side-groups. Thus with the side-groups CH_3, C_2H_5, and C_6H_5 in the monomer units, adhesion is highest in a polymer containing methyl side-groups, and lowest in one containing phenyl side-groups.

It is interesting that not only do long branches not diminish adhesion but they tend to increase it[71,72]. This is because every sufficiently long branch of a linear macromolecule can act as a separate chain, capable of independent diffusion.

The diminished tendency of polymers to self-diffusion and interdiffusion with increase in the number and volume of sufficiently short side-groups in their molecules agrees well with the fact that the presence of such groups causes a decrease in intensity of micro-Brownian motion. This fact has been shown especially clearly in recent investigations of the segmentary motion of polymer chains in which use was made of nuclear magnetic resonance[73–78].

Effect of Polar Groups

The greater the dipole moment of the diffusing molecule and of the polar groups in the polymer, the smaller is the diffusion coefficient, since detachment of the moving molecule from the group in the polymer with which it is interacting is more difficult. This explains, for example, the well-known fact that the molecules CH_3CHCl_2 and CH_2ClCH_2Cl, which are identical in mass and composition, diffuse in polystyrene at different rates, the polar molecule moving more slowly than the non-polar molecule. Furthermore, increase in the dipole moments and in the number of polar groups in the polymer tends to increase the density of the latter, which also has an unfavourable effect on diffusion.

A decrease in diffusion coefficient with increasing polarity of the polymer in which diffusion is occurring has been observed many times. Van Amerongen[68] showed early that the diffusion of gases in butadiene–acrylonitrile polymers falls with increase in the number of nitrile groups in the copolymer molecules. He also established that the activation energy of diffusion is directly proportional to the cohesive forces acting between the polymer macromolecules. Pavlov and Lorant[79] confirmed a marked drop in the diffusion coefficient of water in poly(vinyl acetate) as

the latter was gradually hydrolysed to poly(vinyl alcohol). Experiments by Malinskii and his coworkers [80] on the diffusion of monatomic gases through polymer films of differing structure also showed that increase in the energy of interaction between macromolecules results in a continuous diminution in the diffusion coefficient.

Voyutskii *et al.*[66] also found, in an investigation of the adhesion of butadiene–acrylonitrile copolymers to a polyamide, that the interdiffusion of polymers diminished with increase in the content of polar groups.

The influence of polar groups on the activation energy of diffusion in polymers was studied by Voyutskii and Shtarkh[7], who determined the temperature dependence of the self-adhesion of butadiene–acrylonitrile copolymers containing different proportions of the nitrile. The apparent activation energy E was found to be higher the greater the nitrile content of the polymer (Table 1). An explanation is that the increase in polarity involves an increase in the energy necessary to ensure that the diffusing segment shall penetrate the microvoid between the molecules.

Effect of Molecular Unsaturation

There are indications[53,81] that molecules containing double bonds encounter less resistance than do molecules of the corresponding saturated compounds to movement through a polymer. Bent[81] attempts to explain this by the increased rigidity of the molecule accompanying increase in unsaturation; with increased rigidity the probability of the simultaneous translational motion of all parts of the molecule also increases. The latter should favour more rapid movement of the molecule. Vasenin[59], who made a detailed study of the relation between unsaturation and diffusibility of a molecule, considers that the smaller drag on an unsaturated molecule compared with a saturated molecule is due to a decrease in the number of individual kinetic units responsible for transferring momentum to the macromolecules of the medium. This can be seen, for example, from a consideration of the motion of the molecules CH_4 and C_2H_4. The latter contains two carbon atoms, but linked by a double bond and representing a single kinetic unit. The drag on methane and ethylene molecules can be written

$$F_{CH_4} = \frac{1}{2} mv\nu, \qquad (7)$$

$$F_{C_2H_4} = \frac{Mm}{M+m} v\nu, \qquad (8)$$

where M is the mass of the C_2H_4 molecule, and m that of a monomer unit in the polymer, in this case a CH_2 group, so that $M = 2m$. The ratio of the diffusion coefficient of ethylene $D_{C_2H_4}$ to that of methane D_1 gives

$$D_{C_2H_4} = \frac{3}{4} D_1. \qquad (9)$$

Diffusion coefficients calculated by means of analogous equations agree with the experimental values to within 10%. Hence Vasenin considers the original hypothesis, that the number of kinetic units capable of transferring momentum diminishes when a single bond is replaced by a double bond, as quite reasonable.

Using the above ideas on the mechanism of the resistance offered by the medium to the movement of molecules containing n carbon atoms, Vasenin derived the following general relation between diffusion coefficient D and number of multiple bonds q

$$D = \frac{D_1 (2n-q)}{\sigma^q n (2n-2q)}. \qquad (10)$$

This equation is more general than Eqn.(6), since it allows for the influence on the diffusion coefficient not only of the size and shape of the diffusing molecule but also of its degree of unsaturation.

Eqns.(6) and (10) are, of course, approximate both owing to the simplified scheme adopted in determining the drag on the moving molecule and also because their derivation is based on the assumption that the activation energy of diffusion is independent of the size and shape of the molecule, which is incorrect. Nevertheless, Eqn.(10) can be used to calculate approximate values of the diffusion coefficients of chain segments of different length in polymers of the same nature. Table 2 gives similar values calculated for diffusion in natural rubber. It is readily seen that the calculated values are comparable with values determined experimentally by Bresler and his coworkers for the diffusion coefficient of polyisoprene in natural rubber.

Experiment has shown that unsaturation in the polymer molecules in which diffusion occurs also tends to increase the diffusion coefficient. Auerbach *et al.*[19] showed, in a detailed study of this question, that the diffusion coefficient of octadecane had fallen by 47–61% after saturation of unsaturated polymers by hydrogenation. They found that the activation energy of diffusion in unsaturated polymers is 8–9 kcal mole^{-1}, compared with 10–11 kcal mole^{-1} in saturated polymers.

The presence of double bonds in a macromolecule substantially increases the probability of microvoids being formed in the bulk of the polymer, owing to local rigidity of the bonds and the resulting steric hindrance to the production of closer packing.

The comparatively slight changes in the density of unsaturated polymers resulting from their hydrogenation show, however, that the hindrance to diffusion is not confined to the creation of more favourable conditions for a

TABLE 1.

Nitrile content of copolymer, %	E, cal
19.6	4760
28.0	8670
36.9	16590

TABLE 2. Approximate diffusion coefficients of linear chains and segments of natural rubber.

M	D(40°), cm^2 s^{-1}	D(60°), cm^2 s^{-1}
68	$3.3 \cdot 10^{-7}$	$7.4 \cdot 10^{-7}$
138	$0.7 \cdot 10^{-7}$	$1.6 \cdot 10^{-7}$
1360	$0.7 \cdot 10^{-9}$	$1.6 \cdot 10^{-9}$
13 600	$0.7 \cdot 10^{-11}$	$1.6 \cdot 10^{-11}$
136000	$0.7 \cdot 10^{-13}$	$1.6 \cdot 10^{-13}$

denser packing of the macromolecules. The fact that the diffusion coefficient of octadecane in completely hydrogenated polybutadiene, polyisoprene, and butadiene–styrene copolymer was still far greater than the diffusion coefficient in polyisobutylene indicates that peculiarities of the carbon skeleton of the macromolecule are of great significance for diffusion processes in polymers.

Effect of Relative Ordering of Molecules and of Phase Constitution of Polymer

All that has been said above about diffusion has applied mainly to typical unvulcanised rubbers, *i.e.* to polymers having the least clearly defined ordering of the chains. However, the view that a large number of elastomers contain, in addition to separate molecules, supermolecular structures — bundles, ribbons, lobes, and other formations — consisting of individual ordered molecular chains, is now finding increasing acceptance. It is clear that the above concepts must be suitably amended for such polymers.

Formation of such structures must result from orientation of the molecules, which can be achieved only by movement of molecular chains or segments thereof in the bulk of the polymer. In either case, of course, the process is none other than diffusion. The breakdown of supermolecular structures, which usually possess considerable lability, is also a diffusion process. It may be supposed that, under certain conditions, whole bundles and even more highly organised structural units may diffuse within the polymer. The possibility of such phenomena in the self-adhesion and the adhesion of polymers is mentioned in the literature [16,71]. Furthermore, since each bundle is a fluctuating structure with a long but nevertheless finite life, molecules may well be transferred, in part or in whole, from the surface of one bundle to another. Clearly, such molecular transfer must always be a diffusion process. Shtarkman *et al.* [82] were the first to point out the possibility of such a phenomenon in the formation of a self-adhesion bond between two portions of polymer containing supermolecular structures and brought into contact. It may also be suggested that a similar process should occur in adhesion, the sticking together of different polymers. One fundamental feature should be observed: apart from the main condition making adhesion possible, which is the capacity of the polymers for thermodynamic compatibility, in this case structural or conformational compatibility is also necessary.

Unfortunately, too few data are yet available to make possible a more detailed examination of diffusion processes in polymers containing supermolecular structures.

Far more experimental information is available on the way in which diffusion in polymers is influenced by the mutual ordering of the macromolecules, involving such factors as the compactness of their packing (density of the polymer), the degree of orientation of the molecular chains, the phase constitution of the polymer, etc.

The density of a polymer can be regarded as an indication of the volume of microvoids present. The diffusion of simple molecules or segment of macromolecules in a polymer must obviously be linked with the tendency for microvoids to be formed in the polymer, with the volume of such microvoids, and also with the passage of the diffusing kinetic units from one microvoid to another.

The relation between the diffusion coefficient of octadecane in various polymers and their density was investigated by Auerbach *et al.* [19], who showed that in general the rate of diffusion decreases with increase in density of the polymer, the decrease being more rapid with saturated than with unsaturated polymers.

Brandt [64] also found a decrease in diffusion coefficient with increase in polymer density for the diffusion of ethane into polyethylene. He assumed that such diffusion occurs only in the amorphous regions, the diffusion coefficient being about 3×10^{-6} cm^2 s^{-1}.

Tikhomirova *et al.* [80] showed that an increase in the packing factor, *i.e.* an increase in the proportion of the space occupied by the substance of the polymer, decreases the diffusion coefficient for a gas.

The effect of the proportion of crystalline phase in a polymer on the rate of diffusion of gases through it was studied in detail by Van Amerongen [68], who showed that crystallisation causes a decrease in the diffusion coefficient.

Auerbach *et al.* [19] found high activation energies for diffusion of organic substances in crystalline polyethylene and balata, 12.2 and 16.3 kcal mole^{-1} respectively. Klute [83] also found that the activation energy of diffusion increases with increasing content of crystalline phase in the polymer. The low diffusion coefficients and high activation energies of the process in crystalline polymers are obviously explained by the denser packing of the macromolecules in such polymers. On the other hand, Zhurkov and Ryskin [43], as well Jeschke and Stuart [84], observed an increase in activation energy when polymers passed, with rising temperature, from the crystalline and vitrified states into a condition of rubber-like elasticity. The first two workers explain such a relation, which does not fit our usual ideas on diffusion in polymers, by the temperature dependence of activation energy. Jeschke and Stuart are inclined to explain this phenomenon as due to the occurrence of diffusion mainly in regions of the crystalline phase having a distorted structure or at the interface between amorphous and crystalline phases.

Many workers have investigated molecular motion in crystalline and crystallising polymers by the method of nuclear magnetic resonance, determination of dielectric relaxation, etc.

Slichter [76,77] assumes that the motion of segments of macromolecules in polymers consists of a combination of different types of movement, the motion in crystalline regions of polymers differing in nature from that in amorphous regions. In the former, only vibrational motion of the carbon atoms about the C–C bonds is, obviously, possible. In amorphous regions, however, the segments can undergo rotation and translation, the extent of which is determined by the crystallinity of the polymer: Kline *et al.* [74] showed that increase in size of the crystalline regions produces additional stresses limiting the mobility of the polymer chains in the amorphous regions.

A rise in temperature results in fusion of the crystallites, with increased mobility of the molecular chains. Woodward *et al.* [75] investigated the motion of segments of polybut-1-ene macromolecules, and established that, within definite temperature ranges, large portions of the macromolecules undergo cooperative movement between the crystallites. Such movement is, of course, prevented by a high degree of ordering and denser packing of the macromolecules. For this reason the mobility of the segments in iso-

tactic polypropylene is lower than the corresponding mobility in the atactic polymer [73,76].

The movement of the segments is limited also by various interactions between neighbouring macromolecules. Thus in polyamides this will be represented by bonds between CONH groups in neighbouring chains; and in butadiene–acrylonitrile polymers by bonds between CN groups, etc.

Any weakening of intermolecular interaction in some way (by rise in temperature, introduction of non-polar groups into the molecule, etc.) results in more vigorous movement of the segments in these polymers [85].

Effect of Presence of Three-Dimensional Structures in the Polymer

The influence of the degree of cross-linking of polymers on their permeability to gases was studied in detail by Barrer and Skirrow [53], who showed that the diffusion coefficient falls with increase in the quantity of combined sulphur. Similar results were obtained by Aitken and Barrer [37] for specimens of rubbers which had been cross-linked with peroxides. It was found that the diffusion coefficient diminishes with increasing degree of cross-linking of the polymer, varying in direct proportion to the length of chain between two adjacent cross-links.

Malinskii *et al.* [80] have investigated the influence of the cross-linking action of radiation (^{60}Co γ-rays) on the diffusion of gases in various polymers. They showed that the rate of diffusion of gases in irradiated polyethylene, polyamides, and SKS-30 rubber is lowered, probably because of the formation of cross-links between the macromolecules.

Auerbach *et al.* [19] investigated the diffusion of octadecane into natural rubber which had been vulcanised with dicumenyl peroxide. Instead of the expected fall in diffusion coefficient with increasing degree of cross-linking, diffusion was found to be improved at low degrees of cross-linking. It is probable that under these conditions lattice defects (free ends and interlocking loops) play an especially large role, destroying the compactness of the polymer structure and favouring the formation during vulcanisation of larger microvoids than in the crude rubber.

It is interesting that a similar relation had been found earlier by Voyutskii and Shtarkh [7] in an investigation of the self-adhesion of natural rubbers with different degrees of cross-linking. These workers explained the increase in self-adhesion at the start of vulcanisation by the increased extent of diffusion resulting from breakdown of the intermolecular bonds or even of the macromolecules themselves owing to oxidative degradation. Further vulcanisation produces a three-dimensional structure with a marked decrease in diffusibility of the cross-linked polymers.

Raevskii and Voyutskii [86] have studied the decrease in adhesion produced by the cross-linking of polymer molecules.

Bresler *et al.* [12] have used the radiometric technique described above to study directly the effect of the cross-linking due to vulcanisation on the interdiffusion of polymers. With polyisoprene of molecular weight 11 000 the diffusion coefficient was considerably lower in vulcanised than in unvulcanised natural rubber. Bresler explains this by the cross-linking of macromolecules into a three-dimensional network during the vulcanisation of rubber, the cells of this structure offering further resistance to diffusion.

The sharp fall in diffusibility accompanying vulcanisation of a polymer is associated with immobility of comparatively large sections of the molecular chain. This is indicated by the very slight influence of vulcanisation on the ability of short chains and individual groups to take part in the ordinary molecular motion, as revealed by nuclear magnetic resonance [77].

VI. IMPORTANCE OF SELF-DIFFUSION AND INTERDIFFUSION IN THE PROCESSING AND APPLICATION OF POLYMERS

Significance of Self-Diffusion for the Viscoelastic Properties of Polymers

Since diffusion phenomena underlie viscosity [22-30], the role of self-diffusion in the flow of polymers is obvious. This problem which has been studied in detail by both Soviet [87-89] and foreign [29,90,91] investigators, is thoroughly discussed in many present-day monographs and textbooks [92-95], and need not be considered here. However, the self-diffusion of segments is of great significance also for the elastic properties of polymers, as follows from the entropy character of rubberlike elasticity.

The diffusion character of rubberlike elasticity follows from the work of Frenkel' and also of Kargin and Slonimskii published during 1938–1949. The diffusion theory of the viscoelasticity of polymers was developed abroad by Kirkwood [96], Rouse [97], and Zimm [98]. Quite recently Mooney [99] has given a detailed analysis of this theory and suggested the appropriate mathematical treatment.

The diffusion theory of viscoelasticity predicts a distribution of relaxation times which agrees quite well with experiment. According to the suggested mechanism, when the statistical distribution of conformations of chain molecules is disturbed under the influence of an external load, the new conformations are not initially in the statistical equilibrium corresponding to this load. As a result, they gradually change towards the establishment of a new equilibrium. These changes in conformation are a consequence of the thermal kinetic motion of individual segments of chain molecules, *i.e.* of constrained diffusion. After removal of the applied load, the polymer specimen contracts owing to the reverse diffusion of the segments, due to their thermal motion and the tendency of the molecule to adopt the most probable conformation.

The theory ignores purely viscous resistance to deformation, which is typical of a liquid and which arises from simultaneous relative motion of chain segments. However, this resistance is usually extremely small compared with viscoelastic forces resulting from changes in entropy. Where it cannot be neglected, it can readily be allowed for in the modern theory.

Significance of Self-Diffusion for the Self-Adhesion of Polymers and for Their Processing

The phenomenon of self-adhesion, which underlies several technically important processes in the treatment and application of polymers, consists essentially in self-diffusion. Zhukov and Talmud [100] were the first to pay attention to self-adhesion. Later it was studied by several Soviet and foreign scientists [1,2,4-7]. A detailed description

of the phenomenon and a comprehensive bibliography will be found in a monograph on the subject[3].

The correctness of the view that self-adhesion results from the self-diffusion of macromolecules or their segments is supported by the dependence of self-adhesion on the time and temperature of the contact[2-7], by the closeness of its activation energy to those of diffusion processes, and by the characteristic influence of the size, shape, and structure of the polymer molecules on self-adhesion, as discussed above.

Of course, the concept of self-adhesion as caused by the interlacing of separate chain molecules by diffusion is to some extent simplified. It is more or less applicable only to those high polymers whose structure corresponds to a "felt" model. When bundles or structures of higher order are present in the polymer, the phenomenon of self-adhesion is considerably more complicated, although its primary cause remains self-diffusion. It may be supposed[82] that in this case self-adhesion will consist, in effect, mainly in the partial transfer by diffusion of macromolecules from bundle structures in one polymer layer to similar structures in the other layer.

Self-adhesion, and hence self-diffusion, form the basis of such important processes in polymer technology as milling, mastication, and the processing on mixing equipment in general. First of all, the flow of a polymer between the rollers of a mill or the rotors of a mixer is ultimately due, like any flow of polymers, to the diffusion of both molecular segments and entire molecules. Furthermore, if self-diffusion did not exist, processing of a polymer on mixing machinery, for example the milling of raw rubber or of vulcanised stock, would yield crumbs or sheets of loosely attached layers of the mixture, instead of a coherent and durable mass. It is only as a result of the self-diffusion of macromolecules that the thin layers of raw rubber leaving the gap between the rollers adhere firmly to one another and form a thick, solid sheet. Unfortunately, as far as we are aware, no one has studied the role of self-adhesion in the processing of mixtures using mixing equipment.

Self-diffusion phenomena are also of great importance in calendering. In particular, the diffusion of macromolecules and segments thereof while the mixture is between the rollers of the calender is explained by the anisotropy of the mechanical properties of the mixture, the so-called calender effect. Diffusion also explains the diminution in the calender effect when the mixture is stored, and its complete disappearance when the calender mixture is heated[101].

The manufacture of rubber goods and the covulcanisation of rubber stock are also based on self-adhesion and hence on diffusion. In the latter case, diffusion of macromolecules takes place during the first period of vulcanisation, when the temperature is still quite high but cross-linking by the formation of sulphur bridges between the molecules has not yet occurred[102]. Sometimes, special substances are added to polymers to increase self-adhesion[103,104].

Diffusion of macromolecules is responsible also for the firm bonding of the layers in multilayer rubber and rubber-fabric goods made both with and without the use of rubber adhesives. In both cases the article is vulcanised after assembly, which further strengthens the self-adhesion bond.

Diffusion is equally important in the welding of thermoplastics[105]. The welding of transparent poly(methyl methacrylate) and some other thermoplastics exhibits all the characteristics of self-adhesion[45-47]. At temperatures corresponding to a state of rubberlike elasticity, when only chain segments can diffuse, the strength of a welded seam in poly(methyl methacrylate) hardly ever reaches the cohesive strength of the material. At temperatures above that for transition to a state of viscous flow where complete macromolecules can diffuse, the strength of a weld is usually equal to that of the massive material.

For this transparent plastic, when the polymer chains were initially oriented with the macromolecules in the plane of the weld, far greater strength was obtained, on welding at temperatures corresponding to a state of rubberlike elasticity, than with the molecules oriented perpendicular to the plane of the weld. This is because in the former case interdiffusion and interlacing of the macromolecule segments take place readily, whereas in the latter case the diffusion of segments parallel to the direction of orientation is extremely difficult.

Diffusion also underlies the moulding of articles from powders or granulated thermoplastics[106,107]. It has been established that the sintering properties of moulding powders deteriorated with increased content of polar groups in the polymer, with increase in the molecular weight of the latter, and with decrease in the plasticiser content. This is completely consistent with the effect of these factors on self-adhesion. It has also been shown that powdered "cross-linked" polymers are incapable of complete irreversible sintering. The explanation given[108,107] for this fact is that the presence of cross-links raises the flow point of the polymer, ultimately to above the decomposition temperature. In our view this is due to the presence of bonds between the molecules, which prevent interdiffusion of the latter.

In the production of goods from moulding powders the interesting fact has been observed that increasing the pressure above a certain high value impairs the solidity of the specimen and lowers its strength. This has been explained by the increase in rigidity of the thermoplastic macromolecules with increase in pressure, which, of course, impairs their capacity for self-diffusion.

In conclusion we may note that self-diffusion and self-adhesion explain the formation of films from dispersions of elastomers, natural and synthetic latices. All attempts to explain film formation in such systems by simple coalescence of particles[108-110] have proved unsuccessful, as one of us has shown[111]. The production of continuous, stable, and water-resistant films by the simple drying of aqueous dispersion of elastomers is possible only as a result of the interdiffusion of macromolecules belonging to adjacent particles in the film. Dispersions whose polymer phase is in a vitreous state form a powder, not a continuous film, on being dried. However, such dispersions can yield continuous films at a high temperature, when the polymer passes into a state of rubberlike elasticity or of viscous flow and when interdiffusion becomes possible.

The mechanism by which a continuous film is formed from a dispersed elastomer differs from ordinary self-adhesion only in the fact that a layer of stabiliser is usually present on the surfaces of the dispersed particles, which complicates diffusion. Such stabiliser either remains in the film as discrete inclusions or a network, conferring heterogeneity on the film, or else it dissolves in the polymer. In the latter case the stabiliser may even favour diffusion and the formation of a homogeneous film,

owing to its effect in swelling and softening the surface layers of the polymer globules. It is the presence of stabilisers on the surface of the particles in a dispersion and their differing behaviour in film formation which explain the multiplicity of microstructures possessed by dispersion films. The mechanism of the formation of films from polymer dispersions has been discussed in several papers [112-115] and also in a special monograph [116].

Self-diffusion plays an important part, of course, not only in the preparation of films by drying but also in their production from latices by gelatinisation [117].

Significance of Interdiffusion of Polymer for Adhesion, the Reinforcing Action of Fillers, and the Compatibility of Polymers

According to the diffusion theory of the mutual adhesion of polymers developed by Voyutskii and his coworkers [42,66,71,118-121], the difference between adhesion and self-adhesion consists solely in the fact that the latter involves self-diffusion — *i.e.* identical molecules diffuse — whereas adhesion involves the interdiffusion of macromolecules of two different types. When one of the polymers is an elastomer, while the other is a rigid-chain polymer, diffusion is usually restricted, of course, to the penetration of macromolecules of the first polymer into the second However, interlacing of the chains occurs in this case, too. It is clear that such an explanation of adhesion is applicable only when these two polymers are to some extent compatible, since it is only under such conditions that interdiffusion is possible. On the other hand, it is well known that incongruous polymers possess poor adhesion to one another, and this case is of comparatively slight practical interest. The importance of the mutual solubility of high polymers for their adhesion was pointed out by Voyutskii [122], who proposed using the adhesion of high polymers to one another as a measure of their compatibility. Later Deryagin [123], who also emphasised the link between compatibility and adhesion, suggested assessing the latter from the former.

The importance for adhesion of the mutual solubility of the components, which is determined mainly by the relative polarities of the high polymers [124], is fully consistent with de Bruyne's well-known empirical rule, according to which strong adhesion is possible only when both high polymers are either polar or non-polar, but is difficult when one polymer is polar while the other is non-polar.

The fundamental difference between the diffusion theory and other theories of adhesion is that the former regards the formation of an adhesive joint as a bulk rather than a surface phenomenon. As a result of diffusion the boundary between adhesive and substrate disappears, and a peculiar kind of junction is formed, representing a gradual transition from one polymer to the other.

Evidence for the diffusion theory of adhesion is provided by the dependence of the strength of an adhesive joint between two polymers on time and temperature. Thus, for example, as in self-adhesion, the strength of the bond increases with duration of contact, tending to a definite limit. However, this increase is far slower in a normally vitrified or even crystalline substrate, probably because diffusion occurs with great difficulty. The diffusion theory finds very good support in the variation of adhesion with the size, shape, and polarity of the high polymer molecules [66,71,119,125-127].

Many facts supporting the diffusion theory of the adhesion of polymers to one another are given in a review [128] and in a monograph [3].

It has recently been argued against the diffusion theory that the diffusion of elastomer molecules into dense polymer substrates, for example regenerated cellulose film, is impossible [129]. To this it must be retorted that, as we have already mentioned, the adhesion of polymers is in effect their mutual dissolution. It is clear that in this case the ends or intermediate segments of an elastomer molecule bearing polar groups can penetrate the regenerated cellulose film in exactly the same way as water penetrates it when the film swells. It must be remembered that very shallow penetration (of the order of 10 Å) is sufficient to increase the adhesive strength many times [130]. Moreover, even if the elastomer as a whole is incompatible with the substrate, certain groups or chain segments in its molecules, which have a similar nature to some portion of the substrate surface, may penetrate the latter (diffuse to a limited depth), *i.e.* a process which can be termed "local diffusion" may take place.

The diffusion theory was put forward in the first instance to explain the adhesion of polymer to polymer. However, it is very likely that diffusion plays an important part also in the adhesion of high polymers to glass, metals, and other surfaces. Experiment has shown [131], for example, that the adhesion of elastomers to glass depends on time and temperature of contact, as well as on the molecular structure of the elastomer, in just the same way as does self-adhesion or the adhesion of elastomers to one another. A possible explanation is that the elastomer molecules diffuse either into the surface layer of the glass or into a thin, comparatively loose film of weathering products. The probability that segments of polymer chain molecules diffuse into the surface layer of glass was first pointed out by Korolev [132]. If, of course, the surface layer contains very fine cracks and pores, several molecules can penetrate simultaneously into these submicroscopic spaces, and then we ought to speak not of diffusion but of polymer flow.

Similar results have been obtained in our laboratory for the adhesion of elastomers to various metal surfaces. The elastomer molecules can diffuse into, for example, a comparatively loose layer of the oxide film which is practically always present on a metal surface. It has been reported [133] that the adhesion of polymers to aluminium sheet is considerably increased by the formation of a thick oxide film on the surface of the latter.

It would be wrong to conclude from this that the sole cause of adhesion is always the penetration of adhesive molecules into the surface layer of the substrate, *i.e.* their diffusion through the interface. This is not always so even in the adhesion of polymer to polymer. Voyutskii [120] and also Morozova and Krotova [134] considered in detail the systems and conditions to which a diffusion mechanism of adhesion is applicable and where adhesion must be explained by other causes, for example, adsorption or formation of an electrical double layer. Even with an adsorption mechanism of adhesion, however, diffusion phenomena may play a large part in the formation of a strong adhesive bond. It has been suggested [135,136], for example, that maximum adhesion occurs when the maximum number of active (polar) groups in adhesive and in substrate come together in the interface. Such coincidence, of course, is not achieved immediately, especially if adhesive and substrate are brought into contact in the absence of solvent, but is accom-

plished by the diffusion of flexible adhesive molecules along the substrate surface, which takes time. Similar arguments can be worked out when adhesion is due to electrical forces. In this case correspondence between electron--donor and electron-acceptor groups is necessary, and is also obtained by the diffusion of adhesive macromolecules along the substrate surface.

In addition to "surface" diffusion, the diffusion, from the bulk of the adhesive to the substrate surface, of macromolecular segments containing active groups can also play an important part in the adsorption or the electrical mechanism of adhesion. Such diffusion, followed by interaction between the groups which have diffused and active groups in the substrate, can also produce a considerable strengthening of the adhesive bond with increasing contact time.

The phenomena accompanying addition of a filler to a polymer are very closely related to adhesion. The mechanical properties of a filled mixture must in some measure resemble those of an adhesive joint, the polymer in the filled mixture obviously representing the adhesive, and the filler acting as substrate. In other words, a filled mixture is essentially an extremely complicated adhesive joint, consisting of a multiplicity of alternating layers of solid substrate (filler) and layers (films) of polymer. If this view is correct, diffusion phenomena at the polymer–filler interface, resulting in increased interaction between the two components of the mixture, should be of as great importance for the reinforcing action, as for ensuring good adhesion. In our view research on these lines might make a very valuable contribution to an understanding of the mechanism of strengthening.

In conclusion we may mention that diffusion is of great significance in the preparation of mixtures of two or more polymers, such as are extensively used in industry [101,137-139]. It is difficult by simple mixing on rollers or other mixing devices to achieve molecular distribution of one polymer in another, even if these polymers are thermodynamically compatible. There is every reason to suppose that, in the case of mutually soluble polymeric components, a homogeneous system can be formed only as a result of diffusion, with mechanical mixing in machines merely contributing to this. The most rapid formation of a homogeneous system is favoured, of course, by all the factors which accelerate diffusion — rise in temperature, decrease in viscosity by addition of solvent to the system, etc.

Diffusion is responsible not only for the formation of homogeneous systems in the case of compatible polymers but also for the production of microheterogeneities in artificially produced mixtures of thermodynamically incompatible polymers. Such diffusion does not usually terminate in the complete separation of the mixture into two macroscopic phases, but, owing to the great viscosity of the system, results in separation of the mixture only within microvolumes, in which are grouped monomer units of similar properties. Such a microheterogeneous system generally remains a single whole, since individual microregions remain linked to one another by long molecular chains [140].

Unfortunately, only the most general ideas can be discussed concerning the role of diffusion in the mixing of polymers and the separation of their mixtures. As far as we are aware, no one has yet undertaken quantitative investigations on this problem.

Value of Self-Diffusion and Interdiffusion for Studying the Properties of Polymers

In conclusion we may mention that investigation of the self-adhesion and the adhesion of polymers, together with the related phenomena of self-diffusion and interdiffusion, can be used to obtain new information on the structure and properties of macromolecules and on the structure of high polymers, since a close and direct link exists between the structure and properties of macromolecules on the one hand, and the self-diffusion or interdiffusion of polymers on the other. Therefore the study of self-diffusion or interdiffusion by any of the methods discussed in the early part of this review can yield valuable information on some problem associated with the properties of macromolecules or of a polymer.

In addition, methods of determining self-diffusion can be employed to investigate internal friction in polymers. The advantage of these methods compared with the usual methods of determining viscosity is that during diffusion no external force is acting on the macromolecules and the latter are not in a stressed condition.

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ELECTROCHEMICAL AND PHYSICOCHEMICAL PROPERTIES OF ALUMINIUM COMPOUNDS IN NON-AQUEOUS SOLUTIONS

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I. INTRODUCTION

The electrochemistry of non-aqueous solutions is mainly still in the initial stage of its development. However, the investigation of non-aqueous solutions of aluminium compounds is in a better position. Such solutions have been investigated rather widely since 60 years ago when aluminium was first separated by electrolysis of a solution of aluminium bromide in ethyl bromide[1]. Some of the solutions studied have found practical use, for example, for coating the uranium rods of nuclear reactors with aluminium[2].

The electrochemical properties of non-aqueous solutions of aluminium halides and their complexes have been considered in sufficient detail in earlier reviews and monographs[3-12], therefore here we will only look at the principal results necessary for a general statement, and also individual phenomena insufficiently stressed by the authors of previous publications.

It is established that a marked increase in electrical conductivity on mixing two weakly conducting components is due to their reaction to form more or less stable compounds[13]. On the other hand, the question as to *what* is the nature of the reaction leading to the formation of particles capable of dissociation and *how* they dissociate, is still not clear in many cases. Attention will also be directed to this below.

Not every complex formed in solution is capable of electrolytic dissociation. For example, the complexes of general composition† $AlCl_3SnEt_nCl_{4-n}$ formed during the dissolution of $AlCl_3$ in benzene solutions of ethyltin chlorides do not dissociate[14]. Similarly, not every conducting complex, even of those consistent with a stoichiometric composition, can be used for electrodeposition of the metal. One of the main questions in this connection is to seek means for *a priori* prediction of the fundamental electrochemical properties of a particular solution. The latter is obviously impossible without knowledge and generalisation of the main relations determining the properties of the solutions formed.

† The following symbols are used in the text: M metal, X halogen, R radical, Me CH_3, Et C_2H_5, Ph C_6H_5, Py pyridine, Ar aromatic hydrocarbon, Sol solution, Slv solvent.

II. HYDRIDE ELECTROLYTE (BRENNER'S ELECTROLYTE)

The electrolyte is prepared by mixing a suspension of LiH in ether or an ethereal solution of $LiAlH_4$ with an ethereal solution of $AlCl_3$.[15-17] The composition of the solution (recalculated on the initial components) can be varied within the limits: $AlCl_3$ 2–3 M, LiH 0.5–1.0 M or $LiAlH_4$ 0.13–0.4 M or above. Under these conditions and in an inert atmosphere a compact, pale silvery Al deposit is obtained at current densities $D_c \leq 5$ A dm^{-2} with current efficiencies close to 100%. The aluminium anodes dissolve with efficiencies which also approach 100%. With $D_c > 5$ A dm^{-2} the quality of the precipitates deteriorates, dendritic growth starts, and the lustre is lost.

The experiments of Brenner and coworkers led them to conclude that the ions Li^+, $AlCl_4^-$, and $(AlCl_3H.ether)^-$ exist in the solution[15]. Actually things are not so simple. The composition of the final products of the reaction of LiH (or $LiAlH_4$) with $AlCl_3$ depends strongly on many factors: an excess of one of the initial reagents, the reaction temperature, the intensity of mixing, the order of addition of the reagents, the dispersion of the LiH, etc. Different reactions which are possible between the initial substances and the products of the primary reactions can take place simultaneously, therefore the actual composition of the electrolyte can be greatly different from the simplest variants.

Finholt and coworkers found that these reactions occur[18,19]:

$$4LiH + AlCl_3 \xrightarrow{Et_2O} LiAlH_4 + 3LiCl, \quad (1)$$

$$3LiAlH_4 + AlCl_3 \xrightarrow{Et_2O} 4AlH_3 + 3LiCl, \quad (2)$$

and that $AlCl_3$ is completely converted into AlH_3. However, when there is an excess of $AlCl_3$ the formation of AlH_3 as a final product is doubtful. Since the electrolytes which are obtained when LiH and $LiAlH_4$ are used are identical as regards their principal properties, reactions of type (2) are rather limited. If the reaction leads to the formation of $LiAlCl_3H$ then it must proceed by the scheme:

$$LiAlH_4 + AlCl_3 \rightarrow LiAlCl_3H + AlH_3, \quad (3)$$

but a large excess of $AlCl_3$ is not required for this, whereas an electrolyte with the necessary properties is obtained only when it is in fivefold to tenfold excess. The course of the reaction according to Eqn.(2) requires a quaternary collision in solution, which is of low probability. A more likely supposition is that reaction (2) occurs in stages, the first being:

$$LiAlH_4 + AlCl_3 \rightarrow LiCl + 2AlH_2Cl. \quad (4)$$

The compound AlH_2Cl is unstable and disproportionates[20-22]:

$$2AlH_2Cl \rightarrow AlHCl_2 + AlH_3. \quad (5)$$

In its turn AlH_3 is able to react with $AlCl_3$ according to the schemes[20-22]:

$$AlH_3 + 2AlCl_3 \rightarrow 3AlHCl_2, \quad (6)$$

$$AlH_3 + AlCl_3 \rightarrow AlH_3 \cdot AlCl_3 \rightarrow AlH_2Cl \cdot AlHCl_2. \quad (7)$$

During this the excess of AlH_3 above that required by Eqn.(7) remains unreacted:

$$2AlH_3 + AlCl_3 \rightarrow AlH_2Cl \cdot AlHCl_2 + AlH_3. \quad (8)$$

Trichlorodialane $AlH_2Cl.AlHCl_2$ was obtained also by the overall reaction[23-44]:

$$3LiAlH_4 + 5AlCl_3 \rightarrow 4AlH_2Cl \cdot AlHCl_2 + 3LiCl. \quad (9)$$

Furthermore, certain studies[25,26] established that in the creation of an effective excess of $AlCl_3$ in the course of reaction (1), an intermediate product AlH_nCl_{3-n} is formed; this is close in composition to trichlorodialane and was separated in crystalline form.

Finally, Couch and Brenner[15] found that in the electrolysis of an ethereal solution of $LiAlH_4$ a black powder is deposited on the cathode; this powder consists of lithium and aluminium. According to their results[15] and ours during the electrolysis of an ethereal solution containing 2–3 M $AlCl_3$ and 0.5–0.75 M LiCl, aluminium is deposited on the cathode with very low current efficiencies. Gillet[27] in general did not observe deposition of aluminium from these solutions. Consequently neither $LiAlCl_4$ nor $LiAlH_4$ as such is responsible for the good properties of the hydride electrolyte.

Evans and coworkers[28] carried out a conductimetric titration of an ethereal solution of $AlCl_3$, saturated with LiCl and without it, by an ethereal solution of $LiAlH_4$ (Fig.1); the equivalent percentage was calculated by the authors[28] by reaction (2). It is evident that as the electrical conductivity of the solution increases as a result of the reaction so the course of the reaction itself is independent of the initial presence of LiCl. A very similar curve is also obtained on titrating an ethereal solution of $AlHCl_2$ by $LiAlH_4$ solution. The presence of maxima is explained by supposing the formation of strongly dissociating compounds according to the scheme:

$$LiAlH_4 + 2AlCl_3 \rightarrow LiCl + [Al_2Cl_5]^+[AlH_4]^-, \quad (10)$$

or by

$$LiAlH_4 + 2AlHCl_2 \rightarrow LiCl + [Al_2H_2Cl_3]^+[AlH_4]^-. \quad (11)$$

Both suggestions are essentially arbitrary and no additional evidence has yet been obtained. The rise in electrical conductivity (κ) after the minimum is explained by a reaction between AlH_3, formed at the completion of the reaction, and the excess of $LiAlH_4$. This agrees with the rise in κ on adding $LiAlH_4$ to an ethereal solution of AlH_3 which has been observed by the same authors[28]. On titrating $LiAlH_4$ solution with $AlCl_3$ solution a curve was obtained with a maximum at 33 equiv.% $AlCl_3$, this maximum being treated as the result of the interaction of $LiAlH_4$ and AlH_3; from 120 to 240 equiv.% the curve runs almost parallel to

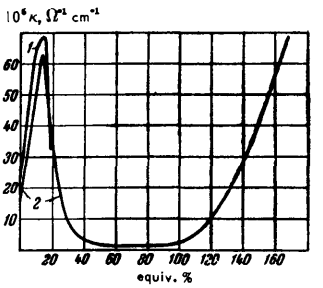


Fig.1. Curves for the conductimetric titration with $LiAlH_4$ of: 1) an ethereal solution of $AlCl_3$ (0.177 M) + LiCl (suspension); 2) ethereal solution of $AlCl_3$ (0.161 M).

the abscissa axis. It would seem that with this excess of $AlCl_3$ reaction (7) must occur. However, the electrical conductivity of trichlorodialane solutions is unknown, hence the reason for this course of the curve is not clear. Solutions of AlH_3, $AlHCl_2$, and $LiAlH_4$ have close electrical conductivities at concentrations of about 0.1–0.4 M, but κ for $AlCl_3$ is about ten times as much.

Hayashi and Ishida[29] investigated the titration of $AlCl_3$ solutions by $LiAlH_4$ solution more carefully and observed a minimum on addition of the first portions of the titrant (Fig.2). They consider the maximum to be linked with reaction (6).

It is interesting that the amount of aluminium which can be deposited from a hydride bath as a high-quality coating is equal to the quantity of aluminium taken in the form of $AlCl_3$ in making up the electrolyte. Since during the operation of the bath the solution does not become depleted in aluminium it was suggested that during its anodic dissolution the aluminium enters the bath as some compound other than that existing in the solution. There is confirmation of this in that a liquid immiscible with the remaining solution gradually accumulates in the anodic space[15,17].

Anodic and cathodic polarisation curves on aluminium electrodes taken using an aluminium wire as comparison electrode, are poorly reproducible for either an ethereal solution of $AlCl_3$ or the hydride electrolyte. These curves also suggest that polarisation is less in the hydride electrolyte, *i.e.* that electrode reactions occur with participation of ions other than those in a solution of pure $AlCl_3$.[15,34]

We consider that reactions (6) and (7) are the most probable, *i.e.* the properties of the hydride electrolyte are connected with the formation of $AlHCl_2$ or $AlH_2Cl.AlHCl_2$, but it is impossible to draw a definite conclusion. It is also not clear whether the presence of LiCl has any significance. The formation of $AlHCl_2$ is supported by Wiberg's results[20-22] [reactions (5)–(8)]; in support of the formation of $AlH_2Cl.AlHCl_2$ there is the analogy with the sesquihalides of aluminium: good aluminium deposits were obtained from solutions of $AlEt_2I$ + $AlEtI_2$ in Et_2O at D_C = 2 A dm^{-2} [30] and from a solution of $AlEt_2Cl$ + $AlEtCl_2$ in xylene at $D_C \simeq$ 1 A dm^{-2} or $AlPh_2Cl$ + $AlPhCl_2$ in xylene at D_C up to 0.33 A dm^{-2}.[31] The answer to this problem may be obtained in an attempt to prepare the hydride electrolyte directly from AlH_3 and $AlCl_3$ with addition of LiCl or without it. Such an investigation has been started in our laboratories.

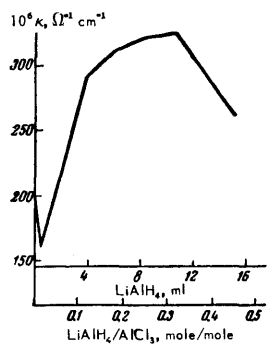


Fig.2. Conductimetric titration on curve for an ethereal solution of $AlCl_3$ (0.53 M) by an ethereal solution of $LiAlH_4$ (0.27 M).

III. ALUMINIUM HALIDES AND THEIR COMPLEXES

The electrochemical properties of solutions of aluminium chloride and bromide and their complexes, mainly with the halides of metals of Groups I, II, and V, ammonium halides, interhalogen compounds, and hydrogen halides in various solvents, have been studied.

A. Binary Systems

The halides of metals of Groups I and II and ammonium halides are almost insoluble in the solvents for which results are given in Tables 4 and 5. $MgBr_2$ is an exception, its solubility in Et_2O being 2.44 wt.% at 20°.[32] A triether compound of $MgBr_2$, stable below 12–13°, is known and its formation is accompanied by liquid immiscibility[33]. Electrolysis of the phase enriched in $MgBr_2$ (2.4 M) showed that hydrogen is liberated at the cathode with an efficiency greater than 80% and CH_4 and CO_2 at the anode; magnesium is not deposited[27].

The data in Tables 1 and 2 characterise the interaction in the MX–solvent systems. The existence of compounds and their compositions are shown from thermal analyses if there are no other indications. Equimolecular compounds are denoted by 1 : 1 and the formula composition is given for non-symmetrical compounds; "eut." denotes a eutectic, and "incongr." an incongruently melting compound.

The electrical conductivity of nitromethane itself[55] is 6×10^{-7} Ω^{-1} cm^{-1} and of the remaining solvents less than 10^{-8} Ω^{-1} cm^{-1}. Individual substances of mixtures with conductivity less than 10^{-8} Ω^{-1} cm^{-1} will subsequently be conventially termed non-conductive. The electrical conductivity of the pure liquid halides MX_3 are: $AlCl_3$ 1.1×10^{-6} (245°);[11] $AlBr_3$ 9×10^{-8} (195°); $AsCl_3$ 1.2×10^{-6} (25°); $AsBr_3$ 1.5×10^{-6} (35°); $SbCl_3$ 1.1×10^{-4} (73°); and $SbBr_3$ 2.4×10^{-4} Ω^{-1} cm^{-1} (99°).[55]

Results concerning the formation of compounds between $AlBr_3$ and benzene, toluene, or xylene are quite contradictory[59,74] and an analysis of them suggests only that there is a relatively weak interaction between the molecules of $AlBr_3$ and these solvents in the liquid phase. Judging from κ, it increases somewhat from benzene to xylene.

During the electrolysis of freshly prepared solutions of $AlBr_3$ in xylene, aluminium is deposited as individual crystallites: it is not deposited from solutions which have been kept for some time after preparation, but tarring occurs at the cathode. Aluminium is not deposited from nitrobenzene and nitromethane and tar is formed at the cathode[11]. On standing, nitromethane solutions become gelatinous[11,57,75]. Aluminium is deposited as a black powder from ether solutions[11].

The electrical conductivity of solutions in ethyl bromide and iodide with less than 10–12 wt.% $AlBr_3$ increases with time[11,77]. Aluminium is not deposited from solutions of such concentration in EtBr [77] but it is deposited from more concentrated solutions. These do not show a change in conductivity on standing and give bright deposits but dendrites are formed if the electrolysis is continued[11]: aluminium is deposited from solutions in EtI only when aluminium anodes

TABLE 1. Physicochemical characteristics of MX_3–solvent binary systems.

Salt	Solvent					
	benzene	toluene	chlorobenzene	nitrobenzene	ethyl bromide	diethyl ether
$AlCl_3$	solubility 0.02 wt. % at 19.9°[32]; does not conduct[11]	solubility 0.039 wt. % at 20.15°[32]; does not conduct[11]	sparingly soluble; does not conduct[35]	1 : 1, 1 : 2, 2 : 1[45,46]; dependence of κ on composition has maximum $1.5 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$ at 14.7 wt. % $AlCl_3$[11]		1 : 1[42,43]; dependence of κ on composition has maximum $1.20 \times 10^{-3}\ \Omega^{-1} \times \times cm^{-1}$ at 33 mole % $AlCl_3$[11]**
$AlBr_3$	weak interaction (*cf.* text) $\kappa = 3 \times 10^{-9}\ \Omega^{-1}\ cm^{-1}$[11]	weak interaction (*cf.* text) $\kappa = 1 \times 10^{-8}\ \Omega^{-1}\ cm^{-1}$ at 35 wt. % $AlBr_3$[11]	eut.[39]; $\kappa = 2.4 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$[35]	1 : 1[32]; dependence of κ on composition has maximum $2.2 \times 10^{-3}\ \Omega^{-1} \times \times cm^{-1}$ at 17.2 wt. % $AlBr_3$[38]	1 : 1[50,51]* dependence of κ on composition has maximum of $3.4 \times \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$ at the ratio $AlBr_3/C_2H_5Br = 0.66$[38,52]**	1 : 1[42,43]; dependence of κ on composition has maximum $1 \times 10^{-3}\ \Omega^{-1} \times \times cm^{-1}$ at 25 mole % $AlBr_3$[11]
$AsCl_3$	–	–	–	–	–	1 : 1 (κ, viscosity, at 0–50°); maximum $\kappa = 2 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$ corresponding to 80 mole % $AsCl_3$[48]
$AsBr_3$	eut.[37]; does not conduct[34]	–	does not conduct[35]	eut.; dependence of κ on composition has two maxima, 1.5×10^{-4} and $3 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$ at 10 and 65 mole % $AsBr_3$; κ and η suggest a 1 : 1 compound[44]	–	dependence of κ on composition has maximum $4 \times \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$ at 95.12 wt. % $AsBr_3$[38]
$SbCl_3$	$C_6H_6 2SbCl_3$[36]	1 : 1 incongr. $C_6H_6CH_3 2SbCl_3$[41]	1 : 1 incongr.[36]	1 : 1[36]; at 53 wt. % $SbCl_3$ $\kappa = 2.4 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$[38]	–	dependence of κ on composition has maximum $2.6 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$ at 86.8 wt. % $SbCl_3$[38]
$SbBr_3$	$C_6H_6.2SbBr_3$[32]; does not conduct[40]	1 : 1 incongr., $C_6H_5CH_3.2SbBr_3$ incongr.[41]; does not conduct[35]	eut.[36]; does not conduct[35]	eut.[36]; dependence of κ on composition has maximum $1.8 \times 10^{-4} \times \times \Omega^{-1}\ cm^{-1}$ at ~33 wt. % $SbBr_3$[33]	–	dependence of κ on composition has maximum $1.25 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$ at 82.3 wt. % $SbBr_3$[38]
$BiBr_3$	sparingly soluble[119]	–	–	eut.[46]; conducts[52]	–	–

* Gorenbein and Danilova's[49] assertion that when $AlBr_3$–C_2H_5Br mixtures are crystallised only the initial components separate should be noted on account of misunderstanding.

** See elsewhere[29,76,77] for electrical conductivity at low concentrations.

TABLE 2. Physicochemical characteristics of $AlBr_3$–solvent binary systems.

Solvent	Properties of binary systems
Xylene	weak interaction (*cf.* text). Freshly prepared solutions have $\kappa = 10^{-4}$–$10^{-5}\ \Omega^{-1}\ cm^{-1}$; at 18° κ increases 70 times in 18 d[11]
Ethyl iodide	dependence of κ on composition has maximum $7.2 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$ at ratio $AlBr_3/C_2H_5I = 0.45$[38]
Dibromoethane	eut.[56]; does not conduct; degree of association in dimer ~50% at 6 wt. % $AlBr_3$ in the solution[11]
Nitromethane	1 : 1 (measurement of dielectric constants of mixtures)[58]; κ increases with concentration and is $1.41 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$ at $c = 1.367$ M[57]

are used[78]. Probably this is due to the formation of an ethylsesquiiodide by the reaction[79]:

$$2Al + 3EtI \rightarrow AlEt_2I + AlEtI_2, \qquad (12)$$

from which Al is then deposited (*cf.* also Keyes *et al.*[30]).

Electrolysis of solutions of $AsBr_3$ and $SbCl_3$ in Et_2O gives good deposits of As and Sb,[80] and Sb is deposited when solutions of $SbCl_3$ and $SbBr_3$ in $PhNO_2$ are electrolysed[57].

The inspissation of solutions and the change in κ during electrolysis over a protracted interval are explained by association of the complexes and by solvation with introduction of molecules of the solvent into the inner sphere of the complex by the scheme[11]:

$$AlX_3 + Slv \rightarrow [AlX_2Slv]^+ + X^-. \qquad (13)$$

Processes of this type are well known for aqueous solutions. Thus the conversion of the green modification of chromium(III) into the violet takes place over a few months[81]. However, in the cases under consideration such an explanation must be used with caution, taking into account the catalytic properties of the aluminium halides, the influence of traces of moisture, etc. Actually, for example, HBr is liberated from dilute solutions of $AlBr_3$ in EtBr and alkenes are formed[50,77]. Therefore in cases not supported by special investigations, the "solvation" hypothesis must be considered as slenderly based, and its application to nitromethane solutions as simply untrue: it was found that with the reduced catalytic activity of $AlBr_3$ on complex formation with alkali metal halides thickening did not take place[75].

According to equilibrium and vapour pressure diagrams[105,106], the hydrogen halides HCl and HBr form unstable compounds with benzene, toluene, and xylene. The electrical conductivity of their solutions in moist solvents at room temperature is of the order of 10^{-4}–$10^{-5}\ \Omega^{-1}\ cm^{-1}$,[108] and in dry solvents κ is close to zero: κ for HX themselves near their boiling points is of the order of 10^{-7}–$10^{-8}\ \Omega^{-1}\ cm^{-1}$.[109]

The compounds ICl and IBr form conducting solutions with nitrobenzene; at 18° for ICl $\kappa = 7.9 \times 10^{-4}$ at ICl : $PhNO_2$ = = 1 : 9.7, and for IBr $\kappa = 3.5 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$ at IBr : $PhNO_2$ = = 1 : 11.28.[110,111] Electrolysis and transport numbers results[112] suggest the formation of the ions $[PhNO_2.I]^+$ and X^-; it was also found that iodine liberated at the cathode is reduced to I^- and then transported to the anode, where it is also deposited as I_2.[113] Hence as a result of the electrolysis, both X_2 and I_2 are liberated at the anode. Values of κ for the compounds themselves at their melting points are: ICl (27.2°) 4.4×10^{-3}, IBr (42°) $4.0 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$.[114]

Table 3 gives information about interactions in the AlX_3–MX_n systems, taken mainly from a handbook[82]. The references to other sources are indicated in the table. The electrical conductivity of the melts is of the order usual for salts with the exception of mixtures with $AsBr_3$ where $\kappa \leqslant 1 \times 10^{-8}\ \Omega^{-1}\ cm^{-1}$.[11]

Complete absence of interaction between AlX_3 and HX is found; for example, on condensing HCl on $AlCl_3$ there is only weak physical absorption[105,115-118]. For 0.1 M $AlBr_3$ in HBr, $\kappa = 2 \times 10^{-7}\ \Omega^{-1}\ cm^{-1}$. Thermal analysis showed that the compounds $AlCl_3.2ICl$ and $AlBr_3.IBr$ are formed[89].

B. Ternary Systems

1. Metal (ammonium) halides–aluminium halides–solvent. Tables 4 and 5 give comparative characteristics for the solubility and electrical conductivity in ternary systems. Three characteristics are given for each system (where the data exist). The first relates to the change in κ with *increase* in the AlX_3 : Slv ratio between the limits 0.05–0.35 at $MX_n : AlX_3$ = const; inc. = increases, dec. = decreases, max.(min.) = passes through the corresponding extremum. The second similarly describes the change in the solubility of MX_n, the number denoting the order of the solubility of MX_n, expressed as a ratio $MX_n : AlX_3$, at AlX_3 : Slv = 0.1–0.3; at other AlX_3 : Slv

TABLE 3. Characteristics of AlX_3–MX_n binary systems (mole %).

MX_n	Characteristics
	$AlCl_3$
LiCl	1 : 1
NaCl	1 : 1, immiscible liquids 0–19.2% NaCl
KCl	1 : 1, immiscible liquids 0–19.1% KCl
KBr	1 : 1, immiscible liquids 0–19.8% KBr
CsCl	1 : 1[85]
NH_4Cl	1 : 1, immiscible liquids 0–20% NH_4Cl[86]
TlCl	1 : 1, $TlCl.2AlCl_3$ (?), immiscible liquids 1.2–14.7% TlCl
AgCl	1 : 1, immiscible liquids 0.7–17.6% AgCl
CuCl	1 : 1
$MgCl_2$	1 : 1 (?)
$SnCl_2$	1 : 1, $SnCl_2.2AlCl_3$, immiscible liquids 1.5–14.3% $SnCl_2$
$SbCl_3$	eut.
$SbBr_3$	eut.
	$AlBr_3$
NaCl	$NaCl.2AlBr_3$, $NaCl.4AlBr_3$, immiscible liquids 0–19% NaCl
KCl	1 : 1, $KCl.2AlBr_3$, immiscible liquids 0–20.9% KCl
LiBr	1 : 1, $LiBr.2AlBr_3$, $LiBr.7AlBr_3$
NaBr	1 : 1, $NaBr.2AlBr_3$, $2NaBr.7AlBr_3$, immiscible liquids 2.6–16.3% NaBr
KBr	1 : 1, $KBr.2AlBr_3$, immiscible liquids 0.4–22.1% KBr
NH_4Br	1 : 1, $NH_4Br.2AlBr_3$, $NH_4Br.3AlBr_3$, immiscible liquids 0.5–20.8% NH_4Br
NaI	1 : 1, immiscible liquids 2–13% NaI[83]
AgCl	1 : 1, immiscible liquids 0–19.2% AgCl
CuCl	1 : 1, $CuCl.2AlBr_3$[84]*
AgBr	1 : 1, $AgBr.2AlBr_3$, immiscible liquids 2.2–17% AgBr
CuBr	1 : 1, compound separated from benzene and ethyl bromide[11]
AgI	1 : 1[84]**
CuI	1 : 1[84]*
$SbCl_3$	exchange with anions
$AsBr_3$	eut.[11]
$SbBr_3$	1 : 1
$BiBr_3$	1 : 1
TlBr	1 : 1, $TlBr.2AlBr_3$, immiscible liquids 0.6–22.8% TlBr
$MgBr_2$	$MgBr_2.2AlBr_3$ (?)
$CdBr_2$	1 : 1
$HgBr_2$	$HgBr_2.2AlBr_3$

* Determined cryoscopically in benzene; results not completely reliable.

** Determined cryoscopically in benzene and ethyl bromide; results not completely reliable.

TABLE 4. Comparative characteristics of the $AlCl_3$–MX_n–solvent systems.

Salt	Solvent			
	chlorobenzene	nitrobenzene	diethyl ether	nitromethane
LiCl			–; 0.5; 7.4×10^{-3} | 0.2	
NaCl		inc.; const. 1.0; inc. 5.9×10^{-3} | 0.15		–; 1.0; inc. 2.9×10^{-2} | 0.135[75]
KCl		dec.; min. (?) 0.6; inc. 4.2×10^{-3} | 0.25[87]		
KBr		–; 0.77; inc. 4.5×10^{-3} | 0.23[38]		
$CdCl_2$		insoluble[53]		
$AsCl_3$			dec. | 0.37–0.71; dec. 9.0; dec. 6.9×10^{-4} | 0.37[90]	
$SbCl_3$			–; 3.0; max. 1.3×10^{-3} | 0.31[90]	
$SbBr_3$	soluble; solution does not conduct	dec.; dec. 4.0; dec. 10^{-3} | 0.137[38]		
RbCl				–; 1.0; inc. 2.7×10^{-2} | 0.05[91]
CsCl				–; 0.59; inc. 2.3×10^{-2} | 0.045[91]
NH_4Cl				–; 0.8; inc. 3.9×10^{-2} | 0.1[91]
NH_4Br				–; 0.9; inc. 2.6×10^{-2} | 0.05[91]
TlCl				–; 0.78; inc. 1.7×10^{-2} | 0.045[91]
AgCl				does not dissolve[91]

TABLE 5. Comparative characteristics of the $AlBr_3$–MX_n–solvent systems.

Salt	Solvent				
	benzene	toluene	xylene	chlorobenzene	nitrobenzene
LiCl	–; 0.8; –[92]	–; 0.8; –[92]	–; 0.6; –[12]		inc. const. 1.0; inc. 3×10^{-3} | 0.04[38]
NaCl	–; 0.5; –[92]	–; 0.5; –[92]	inc.; dec. 0.49; inc. 3.2×10^{-3} | 0.33[96]		inc.; 1.0; inc. 3.2×10^{-3} | 0.04[97]
KCl	–; 0.5; inc. 6.8×10^{-3} | 0.24[93]	–; 0.4; –[92]	–; 0.41; inc. 3×10^{-3} | 0.5[96]		~const.; 0.8; inc. 4×10^{-3} | 0.23[38]
RbCl	inc.; dec. 0.22; inc. 3.2×10^{-3} | 0.22[38,94]				–; 0.8; inc. 4×10^{-3} | 0.23[38]
NH_4Cl	inc.; dec. 0.58 | 0.15; inc. 4×10^{-3} | 0.15[38]		–; 0.44; inc. 3.5×10^{-3} | 0.5[96]		max.; 1.0; inc. 4.5×10^{-3} | 0.25[98]
LiBr	–; 0.7; max. 5.7×10^{-3} | 0.286[38]	–; 0.8; max. 4.7×10^{-3} | 0.297[38]	–; 0.5; –[12]		–; 1.0; inc. 2.8×10^{-3} | 0.23[38,92]
NaBr	–; 0.5; –[92]	–; 0.4; –[92]	inc. 0.3; inc. 1.8×10^{-3} | 0.33[12,96]	sparingly soluble; κ hardly changes[35]	–; dec. 0.7; –[12,100]
KBr	inc.; dec. 0.5; inc. 4.5×10^{-3} | 0.15[11]	inc.; 0.5; inc. 5.3×10^{-3} | 0.45[38,92]	inc.; inc. 0.3; inc. 2.1×10^{-3} | 0.33[96]	sparingly soluble; κ hardly changes[35]	–; inc. 0.86; inc. 3.7×10^{-3} | 0.23[38]
RbBr	–; 0.33; inc. 4.3×10^{-3} | 0.23[38]			sparingly soluble; κ hardly changes[35]	max.; max. 0.77; inc. 3.5×10^{-3} | 0.24[38]
NH_4Br	inc.; inc. 0.5; inc. 7×10^{-3} | 0.23[11]		inc.; inc. 0.3; inc. 3.6×10^{-3} | 0.33[96]		max. ~const. 1.0; inc. 4.8×10^{-3} | 0.25[11]
LiI	–; 0.7; –[92]	–; 0.7; –[92]	–; 0.7; –[12]		
NaI	inc.; dec. 0.7; max. 2.7×10^{-3} | 0.25[11]	–; 0.4; –[92]			max.; dec. 0.5; inc. 5×10^{-3} | 0.105[99]
KI	inc. const. 0.5; inc. 8.4×10^{-3} | 0.25[93]	–; 0.5; –[92]			
NH_4I	inc.; dec. 0.5; inc. 6.2×10^{-3} | 0.23[38]		–; 0.34; inc. 2.4×10^{-3} | 0.33[96]		max.; dec. 0.9; inc. 5×10^{-3} | 0.106[98]
AgCl	–; 0.89; inc. 6×10^{-3} | 0.23[38]				
AgBr	–; 0.61; inc. 5.5×10^{-3} | 0.23[38]	–; 0.8; inc. 4.3×10^{-3} | 0.24[38]		sparingly soluble; κ hardly changes[35]	
CuBr	–; 0.99; max. 4.5×10^{-3} | 0.23[38]	–; 1.0; max. 4.8×10^{-3} | 0.23[38]		sparingly soluble; κ hardly changes[35]	
AgI	–; 0.47; inc. 2.7×10^{-3} | 0.23[38]				
$SbCl_3$					max.; dec. 5.0; dec. 10^{-3} | 0.29[83]
$AsBr_3$	conducts, κ changes strongly with time[11]			very soluble; ternary solution does not conduct[35]	dec.; dec. 8.0; dec. 1.3×10^{-3} | 0.23[38]
$SbBr_3$	–; (1.0); max. 1.2×10^{-3} | 0.37[38]	inc.; –; max. 2×10^{-3} | 0.25[38]		inc.; dec. 2.0; inc. $\sim10^{-4}$[38]	
$BiBr_3$	inc.; max. 1.0; 0.24; max. 6×10^{-4} | 0.24[38]			sparingly soluble, κ hardly changes[35]	dec.; dec. 0.4; dec. 6.7×10^{-4} | 0.23[38]
TlBr	inc.; const. 0.5; inc. 9.5×10^{-3} | 0.24[98]				

Salt	Solvent				
	ethyl bromide	ethyl iodide	dibromoethane	nitromethane	diethyl ether
LiCl	–; 1.12; 0.42; inc. 7.2×10^{-4} | 0.42[38]	inc.; dec. 0.5; dec. 5×10^{-3} | 0.23[102]	–; 0.9; –[104]	inc.; 1.0; inc. 2.3×10^{-2} | 0.04[38]	
NaCl	–; 1 | 0.41; max. 1.1×10^{-3} | 0.41[38]	inc.; dec. 0.21; dec. 5.6×10^{-3} | 0.24[102]	–; 0.6; –[104]	inc.; 1.0; inc. 3×10^{-2} | 0.123[78]	
KCl	–; 0.235 | 0.41; inc. 4.2×10^{-4} | 0.41[38]	inc.; const. 0.1; dec. 5×10^{-3} | 0.23[102]	–; 0.6; –[104]	inc.; 1.0; inc. 2×10^{-2} | 0.04[38]	
NH_4Cl	inc.; inc. 0.15; inc. 3.1×10^{-3} | 0.15[101]				
LiBr	–; inc. 0.9 | 0.29; inc. 9.5×10^{-6} | 0.29[38]	inc.; const. 0.26; dec. 5.5×10^{-3} | 0.24[102]	–; 0.8; –[92]	–; 1.0; –[104]	
NaBr	inc.; max. 1.0; inc. 8×10^{-3} | 0.27[11]	inc.; dec. 0.25; const. 5.7×10^{-3} | 0.24[102]	–; 0.4; –[92]	–; 1.0; –[104]	

TABLE 5. (cont'd)

Salt	Solvent				
	ethyl bromide	ethyl iodide	dibromoethane	nitromethane	diethyl ether
KBr	inc.; dec. 0.3; inc. 2.3×10^{-3} | 0.18 [38]	inc.; dec. 0.12; const. 5.7×10^{-3} | 0.24 [102]	inc.; inc. 0.5 | 0.35; inc. 2.9×10^{-3} | 0.22 [38,98]	–; 1.0; inc. 2.9×10^{-2} | 0.033 [75]	
RbBr	–; 0.04 | 0.24; inc. 2.1×10^{-3} | 0.24 [38]				
NH_4Br	inc.; const. 0.2; inc. 2.9×10^{-3} | 0.15 [101]				
LiI		inc.; dec. 0.45; dec. 4.1×10^{-3} | 0.23 [102]			
NaI	inc.; max. 1.0; max. 1.2×10^{-2} | 0.27 [11]	inc.; inc. 0.2; dec. 4.6×10^{-3} | 0.23 [102]			
KI	inc.; max. 0.13 | 0.18; inc. 5.8×10^{-3} | 0.18 [38]	inc.; inc. 0.1; dec. 5×10^{-3} | 0.24 [102]			
NH_4I	inc.; const. 0.14; inc. 5.4×10^{-3} | 0.15 [101]				
AgCl	–; 0.96 | 0.23; inc. 1.4×10^{-2} | 0.233 [38]	dec.; min. 0.68; inc. 1.2×10^{-2} | 0.24 [38]	–; 0.66 | 0.37; inc. 6×10^{-3} | 0.37 [38]		
CuCl	–; 0.88 | 0.237; inc. 1.2×10^{-2} | 0.237 [38]	dec.; dec. 0.65; max. 8.5×10^{-3} | 0.24 [38]			
AgBr	inc.; max. 1.0; inc. 1.2×10^{-2} | 0.23 [11]	dec.; min. 0.67; inc. 1.2×10^{-2} | 0.23 [38]	inc.; dec. 0.58 | 0.18; inc. 3×10^{-2} | 0.18 [38]		
CuBr	inc.; dec. 0.9; inc. 8×10^{-3} | 0.233 [38]	dec.; dec. 0.73; max. 8.4×10^{-3} | 0.23 [38]	inc.; dec. 0.45; inc. 1.5×10^{-2} | 0.25 [38]		
AgI	inc.; dec. 0.94; inc. 1.4×10^{-2} | 0.23 [38]	dec.; dec. 0.75; inc. 9.5×10^{-3} | 0.23 [11]	–; 0.56 | 0.37; inc. 5.9×10^{-3} | 0.37 [38]		
CuI	–; 0.8 | 0.23; inc. 10^{-2} | 0.23 [38]	dec.; dec. 0.72; max. 6.8×10^{-3} | 0.23 [11]			
$AsBr_3$	inc.; (dec.(?) 5.8; dec. 2.9×10^{-4} | 0.19 [38]				inc.; inc. 3.7; dec. 7×10^{-3} | 0.21 [11]
$SbBr_3$	inc.; 1.8; max. 2.2×10^{-3} | 0.23 [103]				–; 3.8; min. 5.7×10^{-4} | 0.18 [87]
$BiBr_3$	inc.; 0.5; inc. 3.3×10^{-3} | 0.23 [103]				
TlBr	inc.; dec. 0.12; inc. 3.1×10^{-3} | 0.23 [38]				
$CdBr_2$	–; 0.074; max. 1.7×10^{-3} | 0.23 [103]				
$MgBr_2$					–; 0.68; inc. 3.8×10^{-3} | 0.19 [90]

ratios this value is shown after the fraction line. The third characteristic shows how κ changes with *increase* in $MX_n : AlX_3$ at $AlX_3 : Slv = 0.1–0.3$; the number in it expresses κ in Ω^{-1} cm^{-1} at $MX_n : AlX_3 = 0.5$, when solubility permits, or at saturation in MX_n, when $AlX_n : AlX_3 < 0.5$, at the $AlX_3 : Slv$ values shown after the fraction line. Values of κ are given at 18° or 25°; in view of the difference in the compositions of the mixtures the change in κ in this temperature interval is immaterial.

Consideration of Tables 4 and 5 leads to the conclusion that in general the electrical conductivity is of the order of 5×10^{-3} Ω^{-1} cm^{-1}; only in $MeNO_2$ and in certain cases in EtBr does it reach 10^{-2} Ω^{-1} cm^{-1} but for solutions of halides of Group V elements it falls to 5×10^{-4} Ω^{-1} cm^{-1}. The maxima on the electrical conductivity curves express the the rise in viscosity and disappear on introducing the appropriate corrections, as in the AlX_3–Slv binary systems [40,121,122]. In this case the κ curve is monotonic and κ rises with increasing MX_n concentration.

A comparison of Tables 1–5 shows that despite long-standing opinion [11,12] the formation of compounds in the melt is not a condition unambiguously determining the solubility and electrical conductivity in ternary systems. For example, a series of bromides is insoluble in $PhCl–AlBr_3$, AgCl is insoluble in $MeNO_2–AlCl_3$. $AsBr_3$ gives both conducting and non-conducting solutions with $AlBr_3$, etc., *i.e.* there is no sharp correlation between the formation of compounds in the melt and the properties of the ternary mixtures.

A decrease or constancy in the solubility of MX_n on increasing the $AlX_3 : Slv$ ratio and the chosen limits of this ratio give unambiguous evidence of complex formation in the ternary systems. This conclusion follows from an elementary analysis of the nature of the liquidus surface of the ternary systems on the basis of the general principles of physicochemical analysis. Actually in such cases there will always be observed a decrease in the temperature depression on introducing the third component and this is

also an indication of complex formation. Another indication is liquid immiscibility in the system. Under conditions where it exists it is possible to speak of the formation of new particles with molecular fields different from those of the initial components. It figures often in binary systems (*cf.* Table 3), and in the ternary ones it is observed in mixtures of RbCl and TlBr with $AlBr_3 + C_6H_6$.[94,95]

The composition of the complexes existing in the solutions considered is unknown, generally speaking. Cryoscopic, ebullioscopic[11], and refractometric[123] investigations have been carried out in such a way that only complex formation and not the composition of the complexes could be shown. A series of complexes was separated (Table 6) by direct evaporation of the solvent from the mother-liquor previously saturated with MX_n. It is evident from Table 6 that the ratio $MX_n : AlBr_3 = 1$ is observed, as a rule, independently of the solvent.

Taken as a whole, Table 6 shows a quite wide generality in the properties of the ternary systems. The individual differences which exist are more quantitative than qualitative in nature.

The electrolysis results, obtained over a range of compositions to which the data of Tables 4 and 5 relate can be generalised as follows. For the halides of Ag, Cu, Tl, and the Group V metals, in all solvents these metals are deposited on the cathode. For other metals and ammonium in all solvents except $PhNO_2$ and $MeNO_2$, aluminium is deposited on the cathode at $MX_n : AlX_3 \leqslant 0.6$; with $0.6 < MX_n : AlX < 1.0$, aluminium and alkali metal are deposited on the cathode; at $1.0 \leqslant MX : AlX_3$, only alkali metal is deposited (possibly, with traces of aluminium)[11,12]. From $PhNO_2$ and $MeNO_2$ at all values of the $MX_n : AlX_3$ ratio only alkali metal is deposited; tarring occurs at the cathode with ammonium halides, as in the AlX_3–Slv binary mixtures. There are departures from this rule: in the electrolysis of solutions of RbCl and CsCl in $AlCl_3$–$MeNO_2$ cathodic deposition of metal is not observed[91]; deposition of aluminium from solutions of alkali metal or ammonium halides in $AlBr_3$ + EtBr occurs on using platinum anodes only when the $AlBr_3$ concentration in the solution is above 40 wt.%, and at lower concentrations it occurs only on aluminium anodes[102].

In general the cathode material affects only the quality of the deposits but cases are known where the material of the cathode has a more pronounced effect on the process. Thus from solutions of AgX and CuX in $AlBr_3$–EtI silver is not deposited on iron or aluminium but is deposited on copper and platinum, and copper is deposited on all the metals mentioned[78].

The anodic processes have been studied rather less fully. More or less reliable results obtained by chemical analysis of the deposits formed on silver anodes are given in Table 7. One of the difficulties here is the solubility of silver halides in the solutions studied.

An interesting comparison of the results of electrolysis of ternary solutions and melts of the composition $MX_n.2AlBr_3$ and $MX_n.AlBr_3$ was made by Gorenbein and Abramova[128] for M = Li, Na, K, Zn, Pb, Sb, and X = Cl, Br. From melts of mixtures with alkali metal halides aluminium was deposited at low current density, M plus aluminium at high; M is deposited from melts of the remaining salts. Hence the melts behave similarly to solutions in oxygen-free solvents.

It is notable that deposition of alkali metals from ternary solutions in $PhNO_2$ and $MeNO_2$ is not remarkable, since it is known that Li, for example, is deposited in the electrolysis of solutions of LiI in $PhNO_2$, $MeNO_2$, and Et_2O.[129]

Since the decomposition potentials were determined with needle-shaped platinum electrodes and since the electrolytes had random composition and as a rule the electrode

TABLE 6. Complexes separated from solutions in organic solvents.

Solvent	Complex	M.p., °C*	M.p. according to equilibrium diagram, Ref. 82, °C	Reference
Ethyl bromide	$LiBr.AlBr_3$	192	195	124
Nitrobenzene	$LiBr.2AlBr_3.2PhNO_2$	63**	–	125
Benzene	$KCl.AlBr_3.8C_6H_6$	143	171	93
Benzene	$KBr.AlBr_3.nC_6H_6$	187	191.5	93
Chlorobenzene	$KBr.AlBr_3$	173	191.5	126
Benzene	$KI.AlBr_3.nC_6H_6$	120–155***	–	93
Benzene	$TlBr.AlBr_3.2C_6H_6$	182.5	210	95
Ethyl bromide	$2AgBr.3AlBr_3$	180–185***	does not exist	124
Ethyl bromide	$AgBr.AlBr_3$	175	215	126
Ethyl bromide	$CuBr.AlBr_3$	241	does not exist	124
Benzene	$CuBr.AlBr_3$	239	does not exist	125
Toluene	$CuBr.AlBr_3.PhMe$	130–140**	–	125
Benzene	$(BiBr_3.AlBr_3)_2$	–	155	119

* The solvent contained in the complexes distils off on approaching the melting points.

** Melts without loss of solvent.

*** Decomposes in melting.

TABLE 7. Liberation of halogen at the anode.

Binary system	Third component	Halogen liberated	Reference
$AlCl_3$–$PhNO_2$	$SbBr_3$	$1Cl_2 + 5Br_2$	53
$AlBr_3$–C_6H_6	KCl	Cl_2	93
	RbCl	Br_2	127
	NaI	I_2*, $I_2 + Br_2$	11
	KI	I_2	93
$AlBr_3$–PhMe	LiI	Br_2	12
	NaI	I_2*, $I_2 + Br_2$	12
	KI	Br_2	12
$AlBr_3$–C_6H_4Me	LiI	Br_2	12
	NaI	I_2*, $I_2 + Br_2$	12
	KI	I_2*, $I_2 + Br_2$	12
$AlBr_3$–$PhNO_2$	LiCl	Br_2	97
	KCl	Br_2	97
	RbCl	Br_2	97
	NH_4Cl	Cl_2	98
	$SbCl_3$**	$Cl_2 + Br_2$	11
	NaI	$I_2 + Br_2$	99
	NH_4I	I_2	98
$AlBr_3$–EtI	AgCl	I_2	78
	CuCl	I_2	78
	AgBr	I_2	78
	CuBr	I_2	78
	AgI	I_2	78
	CuI	I_2	78

* At low current densities.

** In melts (*cf.* Table 3) and in solution in PhCl complete exchange of anions takes place between $AlBr_3$ and $SbCl_3$ with formation of $AlCl_3$ and $SbBr_3$.[35]

products were not analysed, the decomposition potentials explain little and we do not consider them here, except for two special cases: (1) the determination of decomposition potentials over a wide range of compositions showed that they are strongly dependent on composition[11,100,130]. Judging from these results the deposition of an alkali metal from solutions in EtBr (the sole case of an oxygen-free solvent studied by this method) is possible not only at high concentrations but also at great dilutions: $AlBr_3$: EtBr = = 0.006, MX : $AlBr_3$ = 0.05;[100] this conclusion was not checked by analysis of the electrode products; (2) the decomposition potential in MX–$AlBr_3$–EtI mixtures is almost independent of MX and corresponds to that calculated for AlI_3.[102]

Hence in the electrochemical properties of ternary mixtures attention is again drawn not to individual particular differences but to definite generality in the properties.

2. Hydrogen halides–aluminium halides–solvent. That compounds are formed in the AlX_3–Ar–HX systems has long been known[131], as has been the existence in them of quite high electrical conductivity[132,133], in certain instances reaching 0.01 Ω^{-1} cm^{-1}.[134] Subsequent investigations showed[71,105,135-138] that the most stable compounds of this type under normal conditions have the compositions Ar.HX.Al_2X_6 and (3Ar).HX.Al_2X_6.

In the electrolysis of C_6H_6–HBr–$AlBr_3$ and PhMe–HBr–$AlBr_3$, H_2 is liberated at the cathode and an amount of solvent equivalent to it is collected; a dark product or crystals of $AlBr_3$ (anodes of Pt or Al)[132,133] are formed on the anode. In the electrolysis of xylene solutions of HX–AlX_3 (X = Cl, Br) with platinum anodes aluminium is not deposited; when aluminium anodes are employed aluminium and hydrogen are released together, tar being formed in the electrolyte during the electrolysis process[139]. It is impossible to exclude the possibility that in this case molecules of solvent split off with side formation of aluminium sesquihalides. The introduction of metal halides into a system with liquid immiscibility somewhat reduces the electrical conductivity of the lower layer but the results of the electrolysis are what they would be if the system did not contain HX. In toluene and xylene the introduction of metal halides leads to complete or partial disappearance of liquid immiscibility[134,140,141].

In connection with systems containing HX it is interesting to note the behaviour of the complex $AlBr_3.H_2S$ in C_6H_6. It is readily soluble and a solution containing 53 wt.% of the complex has $\kappa = 3 \times 10^{-4}$ Ω^{-1} cm^{-1}. On electrolysing such a solution hydrogen is liberated at the cathode and bromine and a deposit of unknown composition appears at the anode[146].

3. Interhalogen compounds–aluminium halides–solvent. The electrolysis of solutions and the study of transport numbers showed that from mixtures of ICl–$AlCl_3$ and IBr–$AlBr_3$ with $PhNO_2$ iodine is liberated at the cathode, whereas at the anode Cl_2 (or Br_2 appropriately) appears at the start of the electrolysis, and after some time the same halogens with iodine as impurity. The presence of iodine in the anodic products is explained, as in the binary systems, by reduction of I_2 at the cathode. The anode space is enriched in aluminium and chlorine (or bromine)[111,114]. These data, together with the results of thermal analysis of the IX–AlX_3 systems allowed[89] a formula of the type I^+ $(AlX_4.nIX)^-$ to be proposed for the complexes.

4. Quaternary ammonium salts–aluminium halides–solvent. Very interesting results, especially in comparison with those described above were obtained in investigating EtPyBr–$AlCl_3$ melts and their solutions in organic solvents[143,144]. Molten ethylpyridinium bromide is a good conductor and in the electrolysis of the melt bromine separates at the anode; at the cathode the $(EtPy)^+$ ions are reduced with the formation, probably, of diethyldihydrobipyridyl. In the EtPyBr–$AlCl_3$ system a 1 : 1 compound, m.p. 88°, was observed by thermal analysis; the composition of the eutectics practically coincided with the compositions 2EtPyBr + $AlCl_3$ (45°) and EtPyBr + + 2$AlCl_3$ (-40°). On electrolysis of mixtures containing < 50 mole % $AlCl_3$, $(EtPy)^+$ is discharged at the cathode, and with 50–77 mole % $AlCl_3$ good deposits of aluminium are obtained. Electrolysis of a solution of this mixture in benzene, toluene, or xylene (the aromatic hydrocarbon was added until the appearance of a second layer) showed the same relationship but the optimal limits of the $AlCl_3$ concentration were narrowed to 50–63%. At $AlCl_3$ concentrations above 63%, at the cathode there was deposition of aluminium and simultaneously separation of $AlCl_3$ crystals. On maintaining the optimum concentration of $AlCl_3$ the quality of the deposits was better than in the melt but the permissible current density was higher (0.2 A dm^{-2} and up to 2 A dm^{-2}). Investigation of the ionic transfer in a benzene solution of a mixture with EtPyBr : $AlCl_2$ = 1 showed that the concentrations of chlorine, aluminium, and bromine in the anodic space rose in the proportions 2.85 : 0.92 : 3.10. This and the results of the electrolysis suggested that the decomposition scheme was:

$$EtPyBr \cdot AlCl_3 \rightleftarrows [EtPy]^+ + [AlCl_3Br_2]^-.$$

Good results in electrolysis were also given by solutions in PhCl, Et_2O, RX, and certain other solvents.

Very pure aluminium deposits were obtained from Et_4NBr + $AlBr_3$ melts at $D_C \simeq 7$ A dm^{-2} (the precise composition of the mixture is not given)[30,145].

IV. ELECTROLYTES BASED ON ORGANOALUMINIUM COMPOUNDS

Organoaluminium compounds in the pure liquid state have $\kappa < 10^{-7}$ Ω^{-1} cm^{-1}.[147] However, even about 40 years ago it was established that the complexes $NaAlEt_4$, $Et_4NI.AlEt_3$, and $(iso\text{-}C_5H_{11})_4NI.AlEt_3$, liquids at room temperature, have $\kappa = 10^{-3}$–10^{-4} Ω^{-1} cm^{-1}.[148] Within the last decade compounds of this type were rather widely studied by Ziegler and coworkers[150-154]. It was found preparatively that the alkali metal halides form 1 : 1 complexes with AlR_3‡, some of these complexes being able to add on a second AlR_3 molecule to form MX.2AlR_3. The electrical conductivity of the 1 : 2 complexes, for example, is approximately two orders greater than that of the 1 : 1 complexes and reaches 10^{-2} Ω^{-1} cm^{-1}. Investigation of the stability of the complexes in relation to the removal of AlR_3 in a vacuum, the extraction of AlR_3 by heptane (an indifferent solvent) and to the action of such complex-forming agents as Et_2O and Me_3N, showed that the stability of the 1 : 1 complexes is appreciably greater than that of the 1 : 2 complexes. The general rule of stability, established by Ziegler *et al.*[154], both for the 1 : 1 and 1 : 2 complexes can be formulated very

‡ In this section the symbol R denotes aliphatic radicals.

briefly: the stability of the complexes decreases with a decrease in the ionic radius of the alkali metal cation, with an increase in the ionic radius of the halide ion, and with an increase in the length of the chain of the radical R; first the ability to form 1 : 2 complexes is lost, and then 1 : 1 complexes. The experimental results on the existence of complexes as determined by these conditions is shown in Table 8, where the sign + denotes the formation of 1 : 1 complexes, ++ 1 : 1 and 1 : 2 complexes, and - no complexes. Table 9 shows similar results for the complexes of $AlEt_3$ with alkali metal hydrides and halides. Analogous complexes are formed with the salts of quaternary ammonium bases.

The electrically conducting 1 : 1 complexes were obtained also from MX (X = Cl, Br, I) and AlR_nX_{3-n} (X = F, Cl, n = 1, 2).[154-157] In the case of MF, exchange of halogen takes place[152]:

$$MF+AlR_2X \rightarrow MX+AlR_2F.$$

The tendency to complex formation with MX is expressed by the series $AlEt_3 < AlEt_2Cl < AlEt_2Br < AlEtCl_2$, which agrees with a series for the tendency to complex formation with oxygen- and nitrogen-containing organic Lewis bases[158]. The dependence of the stability of the complexes on the nature of MX is the same as in the preceding case.

The complexes of AlR_2H with MX and MH also conduct electricity but have certain peculiarities[155,159]. Thus $NaAlEt_4$ does not mix with $AlEt_3$, but the complex $NaAlEt_4 . AlEt_2H$ is formed, which is capable of dissolving another 2–3 moles $AlEt_2H$. Investigation of the dependence of electrical conductivity on composition in the $NaAlEt_4$–$AlEt_2H$ and $NaH.AlEt_3$–$AlEt_3$ systems showed their identity, which made it possible to ascribe to this complex the schematic formula $NaH.2AlEt_3$. The existence of a complex richer in $AlEt_2H$ has also been established, namely $NaH.2AlEt_3 . AlEt_2H$. Similarly, $NaF.2AlEt_3$, which does not dissolve $AlEt_3$, dissolves 2–3 moles $AlEt_2H$. The production of mixed complexes of the type $MX.AlR_3.AlR_3'$ and $MX.nAlR_3 . mAlR_2X$ has also been described. It should be noted that although $NaAlEt_4$ and $AlEt_3$ are immiscible when pure, they are able to give a mixed solution in a small amount of toluene.

Several of the complexes described above were electrolysed[155,160-163]. Some examples are shown in Table 10.

Analogous results on the cathodic process were obtained also for the complexes listed in Table 10 in very different solvents: ethers, tertiary amines, tetrahydrofuran, dimethylaniline, dioxan, pyridine, toluene, benzene, etc.

The general rule is that in the electrolysis of fused 1 : 1 complexes or their solutions, there is codeposition of alkali metal and aluminium, the yield of alkali metal increasing with cathodic current density, D_c, and at $D_c > 1$ A dm^{-2} almost pure alkali metal is deposited. On the other hand in the case of the 1 : 2 complexes aluminium is deposited alone at all current densities studied. The latter is not true, however, for all mixtures. Thus in the electrolysis of $NaF.2AlEt_3 + AlEt_2H$ mixtures it was found[159] that at D_c = 5 A dm^{-2} sodium is not codeposited, but at 10 A dm^{-2} the cathodic deposit contains sodium as impurity, rapidly dissolving when the current is switched off.

The anodic process depends on the anode material. When hydride hydrogen does not enter into the composition of the complex, then on using insoluble anodes there is decomposition of the radicals R accompanied by the formation of corresponding organic products (CH_4 and C_2H_6 in the case of R = C_2H_5). When soluble anodes are employed the corresponding alkylmetals are formed, which pass into solution, or if there is immiscibility, with formation of a liquid layer; for example, this occurs on using aluminium anodes in electrolytes of the $NaAlEt_4$ type, in the $NaAlEt_4$ + + $KAlEt_4$ eutectic mixture, or on using lead anodes in $NaF.2AlEt_3$ electrolyte[160,164]. If one believes a patent[165], then such a process is general for the metals of Periodic Groups IA, IIA, III, and IVB. Ziegler and coworkers[161] propose for this process the scheme:

$$AlEt_4^- - e \rightarrow AlEt_4 \rightarrow AlEt_3 + Et, \qquad (14)$$

with subsequent reactions of the free radical with the metal of the anode. The formation of $PbEt_4$ also occurs in the electrolysis of a solution of $AlEt_3$ in Et_2O with a lead anode[166].

TABLE 8.

R	F−				Cl−				Br−			
	Na+	K+	Rb+	Cs+	Na+	K+	Rb+	Cs+	Na+	K+	Rb+	Cs
C_2H_5	++	++	++	++	−	+	+	++	−	−	+	+
C_3H_7	++	++	++	++	−	−	+	++	−	−	−	+
iso-C_4H_9	++	++	++	++	−	−	+	+	−	−	−	+
n-C_4H_9	++	++	++	++	−	−	+	+	−	−	−	+
n-C_5H_{13}	−	++	++	++	−	−	−	+	−	−	−	−
iso-C_8H_{17}	−	++	++	++	−	−	−	+	−	−	−	−
n-C_8H_{17}	−	++	++	++	−	−	−	+	−	−	−	−

TABLE 9. Existence of complexes between MH and MX and $AlEt_3$.

Cation	H*	F*	Cl*	Br*	I*
Li^+	+	−	−	−	−
Na^+	+	+	−	−	−
K^+	+*	+	+	−	−
Rb^+	+*	+	+	+	
Cs^+	+*	+	+	+	
$(C_2H_5)_4N^+$	+*	+*	+	+	−

* These cases have not been verified experimentally.

TABLE 10. The cathodic process during the electrolysis of aluminium complexes of organic compounds.

System	Cathodic process during electrolysis
$Al(C_2H_5)_3.NaC_2H_5$	codeposition of Na and Al; current efficiency of Na deposition increases with D_c
$NaC_2H_5.Al(C_2H_5)_3 + Al(C_2H_5) + + n$PhMe	deposition of Al
$Al(C_2H_5)_2Cl.KCl$	codeposition of K and Al
$NaF.Al(C_2H_5)_3$	codeposition of Na and Al
$NaF.2Al(C_2H_5)_3$	deposition of Al
$NaAl(C_2H_5)_4$–$KAl(C_2H_5)_4$ eutectic	deposition of Na at the Hg cathode

TABLE 11. Dependence of the composition of the anodic gases on the material of the anode. $NaF.2AlEt_3 + AlEt_2H$, 24.6 mole %, 80°, $D_a = 10$ A dm^{-2}.

Anode material	H_2	C_2H_6	C_4H_{10}	C_2H_4
Ag	91.2	8.0	[illegible]	—
Cu	93.5	6.2	[illegible]	—
Brass	79.0	17.6	[illegible]	—
Au	44.0	40.2	[illegible]	2.2
Pd	17.3	68.7	[illegible]	[illegible]
Pt	2.8	51.9	[illegible]	[illegible]
Ni	4.7	55.2	[illegible]	[illegible]
F	3.8	39.4	[illegible]	17.3
C	18.0	55.2	[illegible]	17.8

TABLE 12. Dependence of the composition of the anodic gases at a copper anode on the temperature, anodic current density D_a [not given (Ed. of Translation)], and $AlEt_2H$ concentration.

Temperature, °C	$Al(C_2H_5)_2H$, mole %	H_2	C_2H_6	C_2H_4	C_4H_{10}	C_4H_8
80	21.0	72.6	21.7	4.1	1.4	0.2
80	24.6	93.5	6.2	—	0.3	—
80	33.0	98.0	2.0	—	—	—
80	44.1	99.6	0.4	—	—	—
100	12.0	33.8	53.4	12.2	0.3	0.3
100	19.8	61.7	32.1	5.7	0.3	0.2
100	21.0	88.9	8.9	1.0	1.2	—
100	24.6	96.2	3.2	0.4	0.9	0.3
100	28.8	98.5	1.5	—	—	—
120	12.0	74.2	18.7	5.0	1.5	0.6
120	15.6	93.8	4.5	1.5	0.1	0.1
120	20.7	98.0	1.6	0.2	0.1	0.1

When the complex contains hydride hydrogen the anodic process with insoluble anodes is considerably complicated. The composition of the anode gases appears to be strongly dependent on the anode material, the amount of hydride-containing component, the anodic current density, the temperature, and the agitation of the solution at the anode. Tables 11 and 12 give results of investigation of $NaF.2AlEt_3 + nAlEt_2H$ electrolyte [159]. The primary process must be considered to be the common discharge of H^- and Et^- (from complex anions). On considering the possible secondary reactions proposed by the authors [159], the percentage of hydrogen formed as a result of discharge can be calculated. Such calculations were made and showed that this quantity is the greater the higher the energy level of the unfilled inner orbitals of the metals. For copper, not having unfilled orbitals, the percentage of hydrogen discharged is 96.5%. There is also a symbathic relation between the amount (percentage) of hydrogen discharged and the hydrogen overpotential in aqueous solutions of these metals.

V. THE NATURE OF THE IONS IN NON-AQUEOUS SOLUTIONS OF ALUMINIUM COMPOUNDS

Various authors have expressed different opinions regarding the nature of the ions in non-aqueous solutions of aluminium compounds. These opinions are based, mainly, on electrolysis results and the study of transport numbers. Clearly, however, the use of these data alone cannot give an unambiguous answer to the question proposed, especially if there coexist in the solution several species of ions or if the nature of the ionisation changes with concentration. Only in certain relatively simple cases, namely, for the solutions IX + AlX_3 + $PhNO_2$ and EtPyBr + $AlCl_3$ + C_6H_6, is it possible, in the authors' opinion, to agree without special reservations. At the same time all the material given above relates to compounds of aluminium of the general formulae $AlRR'_{n-3}$, where R and R' are oxygen-free radicals. This makes it possible to anticipate a certain generality in the properties of all solutions, and, although also with caution, to use the method of analogies. Both for the basis of the analogy, and for judging the correctness of one or another hypothesis about the structure, thermochemical data are necessary. These are given below, collected for the systems considered above.

A. Thermochemical Data

We have used handbook data [167-170] in all the thermochemical calculations and subsequently the absence of a reference for the quoted thermochemical or thermodynamic quantity means that it has been taken from one of these sources.

Table 13 gives the heats of reaction of AlR_3 with various substances. They have been recalculated from the original data to the most comparable conditions, using handbook quantities. In addition to the assumptions mentioned in the notes to Table 13, the heats of mixing of AlR_3 with indifferent solvents have been disregarded.

It is evident from Table 13 that the strength of the bonds with one and the same ligand increases in the series:

$$AlEt_3 < AlCl_3 < AlBr_3, \quad (15)$$

and for a given AlR_3 with different ligands, in the order of listing in the table. This confirms and extends the conclusion which was drawn from various studies [40,178-181] on

TABLE 13. Heats of reaction ($-\Delta H$) for AlR_3(gas) + B(gas) = = AlR_3.B (solution in indifferent solvent), kcal per mole AlR_3.

AlR_3	Component B									References
	benzene	methyl bromide	ethyl bromide	nitro-benzene	diethyl ether	benzo-phenone	benzalde-hyde	quinoline	pyridine	
$AlEt_3$	—	—	—	—	37.7	—	—	53.1	48.4	147
$AlCl_3$	13.4*	—	—	46.4 (50.6)*	48.9	57.4	62.6	72.4**	75.0**	64,171—174
$AlBr_3$	14.8***	28.5*	32.8*	57.8*	—	61.3	67.1	—	88.4	68,172—176

* Solution in B.

** The heat of fusion of the complex was taken as 5 kcal $mole^{-1}$ by analogy with the heat of fusion of $Al_2Br_6.C_6H_6$, calculated from results [68,172], neglecting the heat of mixing of this liquid complex with benzene.

*** Solution in C_6H_6. Since $AlBr_3$ is dimeric in C_6H_6, the calculation was made for the reaction:

$$\frac{1}{2}Al_2Br_6(gas) + nC_6H_6(gas) = \frac{1}{2}Al_2Br_6.C_6H_6(solution).$$

The heat of the reaction $AlBr_3$(gas) + KBr(gas) = $AlBr_3$.KBr(liquid) is [177] 87.1 kcal per mole $AlBr_3$.

The heat of fusion of the complex was taken as 5 kcal $mole^{-1}$.

the existence of complexes between AlR_3 and Slv_1 in Slv_2 and between AlR_3 and Slv_2 in Slv_1 in respect of the stability of certain complexes of $AlBr_3$ and $AlCl_3$:

$$\text{for } AlCl_3(NH_3,\ Me_3N,\ Py) > PhNO_2 \gtrsim PhCN^{178}, \quad (16)$$

$$\text{for } AlBr_3(Py,\ MeNO_2,\ Et_2O) > PhNO_2 > SbBr_3 > (EtBr,\ C_6H_6)^{40,178-181}. \quad (17)$$

It was stated above that aluminium is not deposited from binary mixtures of its halides with nitrobenzene and nitromethane, but is deposited from mixtures with ether and KBr. It is also known that good aluminium deposits are obtained from $AlBr_3$–Py mixtures[182]. Hence it also follows from the data of Table 13 that for the possible deposition of aluminium the reduction potential of the ligand is more important than the energy of the bond with the ligand: easily reducible nitrobenzene gives rise to tar formation at the cathode but the more stable pyridine permits deposition of the metal.

Since heats of the aggregation changes enter into the thermochemical cycle, Table 13 is supplemented by Table 14, giving the heats of reaction between the same substances in other states of aggregation§. Comparison of Tables 13 and 14 shows that in the energetic relations complexes of AlR_3 with organic ligands are analogous to complexes with inorganic ligands.

For certain solvents there are no data enabling recalculations to be made analogous to those carried out in compiling Tables 13 and 14. For these, experimental results on heats of solution are given in Table 15, which also includes for comparison some solvents from the previous table. The heats of solution of $AlCl_3$ in benzene and of $AlBr_3$ in benzene, toluene, and dibromoethane are close to the heats of fusion of these salts (8.5 and 2.7 kcal × × $mole^{-1}$ respectively), which is evidence of the weak interaction in benzene and toluene, where the aluminium halides at these concentrations are dimers, and of the considerably greater interaction with dibromoethane,

TABLE 15. Heats of solution of crystalline aluminium and antimony halides, kcal $mole^{-1}$.

Substance	Solvent						Reference
	benzene	toluene	nitrobenzene	ethyl bromide	sym.-dibromoethane	ethyl iodide	
$AlCl_3$	+9.1***		−12.22*				64,172
$AlBr_3$	+1.4	+0.77	−22.3*	−0.95**	+2.15**	−1.85**	172,175,186
$SbCl_3$			−0.72*				172
$SbBr_3$			+0.85*				172

* At a concentration of 1 mole salt per 100 moles solvent, 15°. This quantity is reported[99] to be 16.01 kcal $mole^{-1}$ at a significant $AlBr_3$ concentration.

** At infinite dilution, linear extrapolation[175], ~ 6°.

*** In saturated solution, 25°. In the remaining cases the concentration was ~ 10 wt.% salt, 15°.

TABLE 16. Heats of formation of the complexes in the solid state, $MX(cryst.) + nAlX_3(cryst.) = MX.nAlX_3(cryst.)$.

Composition of complex	$-\Delta H$, kcal $mole^{-1}$	Reference	Composition of complex	$-\Delta H$, kcal $mole^{-1}$	Reference
$LiCl \cdot AlCl_3$	2.66	188	$KCl \cdot 2AlBr_3$	16.9	188
$NaCl \cdot AlCl_3$	6.42	188	$LiBr \cdot AlBr_3$	7.9	177
$KCl \cdot AlCl_3$	12.17	188	$LiBr \cdot 2AlBr_3$	4.9	177
$NaBr \cdot AlCl_3$	3.28	188	$NaBr \cdot AlBr_3$	10.1	177
$KBr \cdot AlCl_3$	10.39	188	$NaBr \cdot 2AlBr_3$	7.0	177
$NH_4Cl \cdot AlBr_3$	16.59	187	$KBr \cdot AlBr_3$	16.0	177
$NH_4Cl \cdot 2AlBr_3$	17.36	187	$KBr \cdot 2AlBr_3$	13.9	177
$NH_4Br \cdot AlBr_3$	13.45	187	$NaI \cdot 2AlBr_3$	7.86	99
$NH_4Br \cdot 2AlBr_3$	15.62	187	$NH_4I \cdot AlBr_3$	11.82	187
$NH_4Br \cdot 3AlBr_3$	16.15	187	$NH_4I \cdot 2AlBr_3$	12.24	187
$NaCl \cdot AlBr_3$	9.93	188	$AgBr \cdot AlBr_3$	13.9	177
$NaCl \cdot 2AlBr_3$	9.15	188	$AgBr \cdot 2AlBr_3$	6.9	177
$KCl \cdot AlBr_3$	14.6*	188			

* Results poorly reproducible (note by authors[188]).

TABLE 14. Compilation of heats of reaction of Al_2R_6 with different ligands.

Reaction	$-\Delta H$, kcal $mole^{-1}$	Reference
$\frac{1}{2}Al_2Br_6(cryst.) + \frac{1}{2}C_6H_6(liq.) = \frac{1}{2}Al_2Br_6.C_6H_6(cryst.)$	1.0	68
$\frac{1}{2}Al_2Br_6(cryst.) + KBr(liq.) = AlBr_3.KBr(cryst.)$	20	177
$\frac{1}{2}Al_2Br_6(cryst.) + (Ph)_2CO(liq.) = AlBr_3.(Ph)_2CO(cryst.)$	24.2	176
$\frac{1}{2}Al_2Cl_6(cryst.) + C_9H_7N(liq.) = AlCl_3 + C_9H_7N(cryst.)$	36.0	171
$\frac{1}{2}Al_2Cl_6(cryst.) + C_5H_5N(liq.) = AlCl_3.C_5H_5N(cryst.)$	42.6	174

§ Direct calculation of the bond energies of AlR_3 with ligands is impossible owing to the absence of data on the heats of sublimation of the complexes. Judging from the heats of evaporation of such compounds as, for example, $AlMe_2Cl.Me_3N$ (11.0 kcal $mole^{-1}$ at 105°[167]) and $AlCl_3.NH_4Cl$ (37.5 kcal $mole^{-1}$ at 290–370°[185]), the heats of sublimation at 25° for different complexes are large in absolute value and differ considerably from one another, which excludes the possibility of their reasonable evaluation.

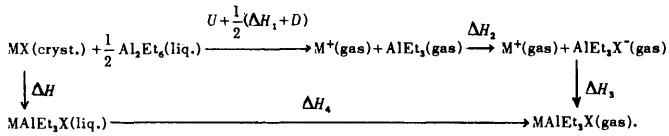
where the association is ~ 50% (Table 2), and consequently, during dissolution part of the heat of dissociation of the dimer is expended¶. The interaction of antimony halides with nitrobenzene is much weaker than that of aluminium halides and this is one of the reasons making it possible to obtain deposits of antimony from nitrobenzene solutions without reduction of the solvent.

Heats of formation of complexes of MX and NH_4X with AlX_3 are collected in Table 16. The complexes for the thermochemical measurements were made by melting appropriate stoichiometric proportions of the components together. According to Table 3, not all of the complexes listed in Table 16 are observed in investigating the equilibrium diagrams, and for some systems equilibrium diagrams are not available. In these cases the authors cited

¶ The heats of solvation of $AlBr_3$ in bromoform, dibromoethane, MeI, EtBr, and EtI have already been calculated[175] as the sum of the heats of solution at infinite dilution and the heat of fusion of $AlBr_3$. This is incorrect, since for an unassociated substance the heat of sublimation, not the heat of fusion, should be taken and for an associated one, such as Al_2Br_6, its state in solution at infinite dilution must be considered and a corresponding fraction of the heat of dissociation of the dimer into the monomer included.

in Table 16 considered that such complexes exist by analogy with known ones, sometimes despite the objective information of the equilibrium diagram. In the absence of other data the heats of formation in such cases should be considered to belong not to individual compounds but to the corresponding mixtures. The information in Table 16 shows that the heats of formation of the 1 : 1 compound with the same component are greater for $AlBr_3$ than for $AlCl_3$, *i.e.* the same as in the case for organic ligands (*cf.* Table 13). In the case of the 1 : 1 compounds for MX the heats of formation increase with a decrease in the crystal lattice energy, and for NH_4X the reverse dependence is observed, but here the equilibrium diagrams for NH_4Cl and NH_4I are unknown. The heats of formation of the complexes (or mixtures) were used for calculations of the decomposition potentials by Thomson's formula[11,12]. Since the heats of solution of the complexes (mixtures) are comparable or exceed (*cf.* Table 19) their heats of formation, such a calculation is inadequate and the conclusions based upon it are not valid. This is one of the reasons why we say almost nothing about decomposition potentials (a second reason is the unreliability of the methods for their determination, which we have already mentioned).

Ziegler *et al.*[154] attempted to obtain a rule for the stability of the MX. $AlEt_3$ complexes by thermochemical means. Certain assumptions were made for this purpose with which it is impossible to agree. Let us consider the thermochemical cycle:



The conditions for the stability of the complex in the liquid state will be

$$\Delta H = U + \frac{1}{2}(\Delta H_1 + D) + \Delta H_2 + \Delta H_3 - \Delta H_4 < 0, \qquad (18)$$

where U is the energy of the crystal lattice MX, ΔH_1 and ΔH_4 are the heats of vaporisation of the corresponding substances, D is the heat of dissociation of Al_2Et_6, and the significance of ΔH_2 and ΔH_3 is clear from the cycle. In the work of Bonitz[147] assumptions are made that: (1) $\frac{1}{2}(\Delta H_1 + D) = 10$ kcal; (2) $\Delta H_4 = 0$; (3) $\Delta H_2 \gg \Delta H_3$; (4) ΔH_2 is inversely proportional to the radii of the anions and by virtue of assumption (3) the same dependence also applies to $\Delta H_5 = \Delta H_2 + \Delta H_3$. Hence the condition for stability is obtained in the form.

$$\Delta H = U + 10 + \Delta H_5 < 0 \qquad (19)$$

and it is possible to calculate ΔH_5 for MX with different X, knowing its value for one salt. ΔH_5 for the KCl complex is taken as this standard, since $AlEt_3$ is quite unstable and $\Delta H \simeq 0$ is assumed for it.

As ΔH is a small difference between large quantities, it is not permissible to disregard the quantities ΔH_1 and ΔH_4. At 80°, $\Delta H_1 = 26$ kcal mole^{-1}; the value of D is unknown, but it is known that for Al_2Me_6 $D = 20.2$ kcal.[189] It is also known that Al_2Me_6 is completely associated in the vapour at 70° and in solutions, whereas Al_2Et_6 is only 12% associated at 150° and is incompletely associated in indifferent solvents, in particular, in C_6H_6 at a concentration of 0.1 mole % it decomposes completely into the monomer in 5 h.[189-191] We can therefore take $D \simeq 10$ kcal. Hence $\frac{1}{2}(\Delta H_1 + D) = 18$ kcal. ΔH_4 is unknown, but it can scarcely be less than 18 kcal (*cf.* the note on p. 130). Hence Eqn. (18) must be used, not (19). Furthermore, ΔH_2 and ΔH_3 are of the same order, therefore assumption (3) is invalid and consequently a basis for calculating ΔH_5 is lost. We require the values of ΔH_2 for the reaction

$$R_1^- + AlR_3 \rightarrow AlR_3R_1^- ,$$

and subsequently we will evaluate them. For this we must assume that $\Delta H_2 \simeq \Delta H_6/3$, where ΔH_6 is the heat of the reaction

$$Al(gas) + 3R(gas) \rightarrow AlR_3(gas).$$

These values of ΔH_2 are given in Table 17. For the formation of AlH_3 from the elements we took $T\Delta S \simeq 6$ kcal, by analogy with reactions of the same type[167], and used the value for the change in free energy in this reaction, -34 kcal mole^{-1}.[192] Now, taking $\Delta H = 0$ for KCl, we obtain $\Delta H_3 \simeq \Delta H_2$, despite arbitrary assumption (3). However, the main opinion of the authors, that under the other different conditions the dominating part is play by the energy of the crystal lattice, must be considered valid, as this follows from Eqn. (19).

According to X-ray analysis[193], at the nodes of the $NaAlCl_4$ crystal there are Na^+ ions and the tetrahedral $AlCl_4^-$ ions. This conclusion was drawn on the basis of infrared spectra of $KAlCl_4$.[194] The same conclusion followed for crystalline $LiAlH_4$ and its solutions in Et_2O, from studies of Raman spectra and infrared spectra[195], and conductimetric titration in ethereal solution[196]. This suggests that the formation of the AlR_4^- ion is a general phenomenon for all reactions of AlR_3 with MR, resulting in the formation of the compound MR. AlR_3. If this is so, then the crystal lattice energies of $MAlR_4$ must decrease as the radius of M increases. Table 18 gives the crystal lattice energies calculated from the data of Tables 16 and 17. As is evident, a fall in U actually occurs, which agrees with the assumption as to the ionic structure of the compounds $M^+[AlR_4]^-$. We note that the crystal lattice energy of $KClO_4$ (calculated by us from heats of solution[167] and hydration of ions[197]), which is constructed of K^+ ions and tetrahedral ClO_4^- ions, is 147 kcal mole^{-1}, which confirms the correctness of the evaluation of the values of ΔH_2. Assumptions

TABLE 17. Heats of the reactions $R^-(gas) + MR_3(gas) = MR^-(gas)$, ΔH_2, kcal × × mole^{-1}.

	AlH_3	$AlBr_3$	$Al(CH_3)_3$	$AsBr_3$	$SbBr_3$
$-\Delta H_2$	82	85	59	46	58

TABLE 18. Crystal lattice energy of MAlBr, kcal mole^{-1}.

Salt	$U + \Delta H_5$	U
$LiAlBr_4$	225	140
$NaAlBr_4$	212	127
$KAlBr_4$	202	117

about the ionic structure of organoaluminium complexes with MX are confirmed also by the decrease in melting point in the series of KCl. AlR_2Cl complexes with an increase in the radical length[157], which can be explained by a decrease in the Coulomb interaction in the lattice as the dimensions of one of the ions are increased. It is also possible to explain from the viewpoint of ionic structure why the halides AlX_3 do not form compounds with HX without the participation of a third component. If for MX U is introduced into Eqn. (19), then in the case for the analogous cycle with HX the ionisation energy for gaseous HX will be introduced; for HCl this is 331 kcal mole^{-1}, for HBr 321 kcal × × mole^{-1}, which exceeds U for the most stable MX crystal lattices by almost 100 kcal†. The presence of a third component makes it possible to compensate this outlay to the first order, evidently on account of interaction with a proton. Benzene and alkylbenzenes release ~25–30 kcal × × mole^{-1} on this account[71,199]. When the third component itself reacts strongly with AlX_3, then no compound is formed between HX and AlX_3, since a further additional expenditure of energy will be required for displacing the strongly bound ligand: thus HBr does not form complexes with $AlBr_3$ in nitrobenzene[200]. On the other hand, in the reaction of gaseous HBr with crystalline Al_2Br_3 and liquid PhMe with the formation of a liquid complex of probable composition $HBr.Al_2Br_6.3PhMe$ 10–30 kcal of heat are released[201] (accurate calculation is impossible on account of the indeterminancy of the composition of the complex and of the experimental conditions).

Tables 19 and 20 give the heats of solution of the $MX.2AlBr_3$ complexes in a series of solvents and MX salts in solutions containing 2 moles $AlBr_3$ per 1 mole MX in the same solvents. The concentrations of the working solutions were not given in the original papers, in any case they were not less than 10 wt.% calculated on $AlBr_3$. The authors note that at such concentrations the heat of solution depends on the concentration comparatively weakly. A distinctive feature is the sharply exothermic nature of the processes of dissolution of the complexes, especially in nitrobenzene. During dissolution in water, only the dissolutions of H_2SO_4 and $MgSO_4$ give comparable effects, -23 and -20 kcal mole^{-1} respectively. At the same time dissolution of crystalline

TABLE 19. Heats of solution of the crystalline complexes, $-\Delta H$, kcal per mole complex.

Composition of complex	Solvent			Reference	Melting point of complex, Ref. 82
	benzene	toluene	nitrobenzene		
$LiCl.2AlBr_3$			39.14	12	equilibrium diagram unknown
$LiBr.2AlBr_3$			50.46	12	131°
$LiI.2AlBr_3$			72.13	12	equilibrium diagram unknown
$NaCl.2AlBr_3$			29.55	12	55°
$NaBr.2AlBr_3$			31.07	12	105°
$NaI.2AlBr_3$			66.70	12	1 : 1, 177° (incongruent)
$KCl.2AlBr_3$	5.6	3.2	30.16	12, 187	83.5°
$KBr.2AlBr_3$	6.85	3.40	34.16	12, 177	95.8°

† The values of U for copper(I) halides given in a handbook[198] are too low by on an average 30 kcal mole^{-1}, for example, 198 kcal is given for CuBr, whereas the correct value (calculated from published data[167]) is 231 kcal mole^{-1}.

TABLE 20. Heats of solution MX(cryst.) + + $(2AlX_3 + nSlv)$(sol.) = (MX + + $2AlX_3$ + Slv)(sol.), $-\Delta H$, kcal per mole MX.

MX(cryst.)	$(2AlX_3 + nSlv)$(sol.)	$-\Delta H$	Reference
KCl	$2AlBr_3+nC_6H_6$	25.30	202
KBr	$2AlBr_3+nC_6H_6$	23.55	186
KCl	$2AlBr_3+n$PhMe	21.64	202
KBr	$2AlBr_3+n$PhMe	18.84*	*cf.* Table in 15
LiBr	$2AlBr_3+n$PhNO$_2$	23.34*	99
NaCl	$2AlBr_3+n$PhNO$_2$	6.68*	99
NaBr	$2AlBr_3+n$PhNO$_2$	6.05*	99
NaJ	$2AlBr_3+n$PhNO$_2$	43.69	99
KCl	$2AlBr_3+n$PhNO$_2$	15.04*	99
KBr	$2AlBr_3+n$PhNO$_2$	16.04*	99

* Calculated by us from data for heats of solution of $2AlX_3 + nSlv$, heats of formation of $MX.2AlX_3$ (Table 16) and heats of solution of $MX.2AlX_3$(cryst.) + nSlv (Table 19).

$AlBr_3$ in benzene and toluene is accompanied by endothermic effects (Table 15). This and the high electrical conductivity of the resulting solutions (Table 5), together with the insolubility of MX in benzene and toluene, make it possible, in our opinion, to suggest with a high degree of probability that the structure of the 1 : 2 complexes is ionic, with a comparatively low crystal lattice energy; the latter is shown particularly by their low melting points (Table 19). A striking fact is that the exothermic effects in the dissolution of KX in benzene and toluene are appreciably greater than in the dissolution of the same salts and NaX in nitrobenzene, the dielectric constant of which is approximately 15 times greater (Table 20). Evidently this can be explained only by the replacement of $PhNO_2$ by X in the coordination sphere of aluminium; in benzene and toluene such replacement does not cause trouble, on account of the low energy of interaction of the solvent with $AlBr_3$ (Tables 13–15). Nevertheless, the heats of solution of KX in toluene are somewhat less (in absolute magnitude) than in benzene, since the energy of interaction of toluene with $AlBr_3$ is somewhat greater than that for benzene (Table 15). The complexes with LiI and NaI are somewhat peculiar; possibly this is connected with the peculiarities of the solvation of the iodide ion.

B. Dissociation Schemes

1. Binary Systems. The most varied dissociation schemes have been suggested. One of these can immediately be shown to be improbable, the others require more detailed consideration. Thus, Wohl and Wertyporoch[203] have given a scheme for a dissociating complex of the form

$$[Al\cdot(BrEt)_n]^{3+}[AlBr_4]^-_3. \qquad (20)$$

The crystal lattice energy of $AlBr_3$ is 1266 kcal mole^{-1} (calculated by us from tabulated data[167,168]). The energy of interaction of aluminium with the ligand does not exceed 100 kcal per bond (*cf.* Tables 13 and 17). The usual coordination number of aluminium is 4, but compounds are known with coordination numbers 5 and 6,[174,204] therefore

we observe that $n = 6$. In the specific case (20), the difference $1266 - [(33 \times 6) + (85 \times 3)] = 813$ kcal must be balanced by the energy of formation of the ion pair (20), multiplied by the degree of association, plus the energy of solvation of its constituent ions multiplied by the degree of dissociation. Since the radii of the ions are large, evaluation of the compensation gives a quantity not exceeding 500 kcal. Hence the minimal deficit, $813-500 \simeq 300$ kcal, is still very large and the possibility of complexes of type (20) being formed must be rejected. A criticism of scheme (20) from a chemical viewpoint has been given by Korshak and Lebedev [206].

By studying the electrical conductivity of the MEt_2–Slv and MPh_2–Slv systems and the exchange activity in these same solvents between M^*Br_2 and MEt_2 (M = Mg, Cd), Strohmeier and Seifert [210] also concluded that the ions M^{2+} are not formed.

Table 21 shows proposed schemes of dissociation based on measurements of transport numbers and electrical conductivity, and on electrolysis results. Some of the data are derived from a brief review on the composition of ions in MX–AlX–Slv systems [207]. The existence of X^- ions is doubtful. Although the energy of solvation of these ions is unknown, it is still reasonable to consider that the total energy of addition of X^- to AlX_3 and solvation of AlX_4^- is greater (in absolute magnitude) than the energy of solvation of X^-. Furthermore, if the dissolution were to proceed by the scheme:

$$AlX_3 + p\,Slv \rightleftarrows [AlX_2 \cdot n Slv]^+ + [X \cdot m Slv]^- + (p - n - m)Slv, \qquad (21)$$

then it would be difficult to explain why halides MX, which are insoluble in solvent, Slv, dissolve in AlX_3 + Slv mixtures with strong exothermic effects (Table 20). The energy of the $X-Al_2X_6$ bonds is unknown. Evidently, one can with sufficient confidence consider $\Delta H_2 < -20$ kcal [presumably $-\Delta H_2 < 20$ kcal is intended (Ed. of Translation)]. Therefore it has to be confined to the assumption that probably both AlX_4^- and $Al_2X_7^-$ ions exist.

A very successful scheme for dissociation in AlX_3–Slv systems has been proposed [175,176,206,211]:

$$[AlX_2 \cdot 2Slv]^+ + AlX_4^-. \qquad (22)$$

The energy for removal of X^- from AlX_3 is unknown. For an estimate it can be taken as equal to the crystal lattice energy of the hypothetical crystal $AlX_2^+.X^-$, 250 kcal × × mole^{-1}, which is clearly much too high. The energy of interaction of AlX_2–2Slv is taken as 70 kcal (Table 13). Then the uncompensated part of the energy of process (22) is 250 - (70 + 85) = 95 kcal. With complete dissociation the total energy of solvation of ions (22) to completion may be of the same order, which permits process (22) to be considered completely permissible.

We can now proceed to some generalisations for binary systems.

(a) *Self-dissociation of AlR_3.* The most probable scheme is:

$$Al_2Br_6 \rightleftarrows AlR_2^+ + AlR_4^- \quad \text{or} \quad \frac{3}{2}\,Al_2R_6 \rightleftarrows AlR_2^+ + Al_3R_7^-. \qquad (23)$$

In the absence of a second component this process is energetically unfavourable, which also determines the low κ of pure liquid Al_2R_6. Confirmation of dissociation with formation of AlR_2^+ and AlR_4^- is found by Bonitz [147] in the reaction:

$$NaAlR_4 + BrAlR_2 \rightarrow \underset{\downarrow}{NaBr} + AlR_3 \cdot AlR_4 \rightleftarrows \underset{\downarrow}{NaBr} + Al_2R_6.$$

In addition he considers that the cations, which contain aluminium, are disclosed by polarographic methods; details of this investigation are not given.

(b) *Dissociation of Complexes.*

$$MR - AlR_3\,(M = M^+, NR_4^+, EtPy^+, X^-;\ R = H^-, X^-, R^-),$$

$$MR + AlR_3 \rightleftarrows M^+ + AlR_4^- \quad \text{or} \quad MR + Al_2R_6 \rightarrow M^+ + Al_2R_7^-\ddagger. \qquad (24)$$

In a considerable number of studies (*cf.*, for example, Refs. 11, 98, 207, and 211) one of the decisive facts in support of the existence of aluminium-containing cations was considered to be the deposition of aluminium on the cathode during electrolysis. Nevertheless, it is well known that often cathodic deposition of a metal takes place from an anion, especially from a complex one (for example, in copper plating or silver plating from cyanide electrolytes; *cf.* also Ukshe [212]), so that the fact of cathodic deposition of metal is still not evidence of the existence of corresponding cations. Actually it is quite difficult to prove the existence of AlX_n^{+3-n} cations in the MX. AlX_3 complexes, and meanwhile at *low* current densities aluminium is deposited, and at *high*, M plus aluminium.

Elementary electrostatic calculations of the stability of ions of various configurations in the MX–AlX_3 systems leads to a conclusion concerning the possibility of existence of the ions M^+, AlX_4^-, and $Al_2X_7^-$. [213]

The formation of AlR_4^- ions is confirmed also by the reaction of replacement of ether in the complex $Et_2O.AlEt_3$ by the ethyl ion:

$$Et_2O \cdot AlEt_3 + NaEt \rightarrow NaAlEt_4 + Et_2O;$$

and an analogous substitution proceeds with LiEt or Py. [214]

In attempting to explain experimental facts on the deposition of metals from MX + $n AlR_3$ mixtures ($1 \leqslant n \leqslant 2$), Ziegler [161] advanced two different hypotheses with which it is impossible to agree.

According to one hypothesis the primary process is the liberation of sodium, which then reacts with $AlEt_3$:

$$Na + 4AlEt_3 \rightarrow 3NaAlEt_4 + Al.$$

TABLE 21. Results of the determination of the composition of the ions in binary systems.

System	Cation	Anion	Reference
NaCl + $AlCl_3$	$[Na.nNaCl]^+$	$AlCl_4^-$ or $AlCl_6^{3-}$	208
KBr + $AlBr_3$	$[K_2Br]^+$, K^+	$Al_2Br_7^-$, $Al_2Br_8^{2-}$	209
ICl + $AlCl_3$	I^+	$AlCl_4^-$	111
IBr + $AlBr_3$	I^+	$AlBr_4^-$	89
$PhNO_2$ + AlX_3 (X = Cl, Br)	$[Al.nPhNO_2]^{3+}$ in dilute solution, $[AlX_2.nPhNO_2]^+$ in more concentrated solution	X^- in dilute solution, AlX_4^- in more concentrated solution, $Al_2X_7^-$ in concentrated solution	207
MeBr + $AlBr_3$	$AlBr_2^+$	Br^-	67
EtBr + $AlBr_3$	$[Al.nEtBr]^{3+}$, $[AlBr.nEtBr]^{2+}$	$Al_2Br_7^-$, $AlBr_4^-$	207
EtBr + $AlBr_3$	$[AlBr_2.EtBr]^+$	Br^-	77

‡ *Note added in proof.* According to X-ray analysis, which the authors learnt about after the manuscript had gone to be typeset, crystals of $KF.2Al(C_2H_5)_3$ are made up of K^+ and $[Al_2Et_6F]^-$ ions [236].

This hypothesis is contradicted by experiment in the following respects: (*a*) the high degree of purity of cathodic aluminium at $n = 2$; (*b*) the low bath potential, 0.3–1 V at an interelectrode distance of 3 cm; (*c*) the low probability of existence of a notable quantity of free $AlEt_3$, particularly in the case $n = 1$, when deposition of aluminium at low current densities is observed.

According to the other hypothesis the deposition of aluminium proceeds during the discharge of cations Al^{3+}, AlR^{2+}, and AlR_2^+, the source of which Ziegler considers to be partially uncombined AlR_3. What was said above concerning the possibility of existence of Al^{3+} ions evidently also applies in essence to the existence of AlR^{2+}. As for the dissociation of unbound $AlEt_3$ with the formation of AlR_2^+, there is no reason which could explain why such a process should intensify in $MX.AlR_3 + AlR_3$ mixtures in comparison with pure AlR_3 to such a degree that κ for the mixture becomes two orders of magnitude higher than for $MX + AlR_3$ mixtures with $n = 1$ and six orders greater than for pure AlR_3. Furthermore this hypothesis also cannot explain the deposition of aluminium from mixtures at $n = 1$.

The regularity in the deposition of aluminium from $MR–AlR_3$ mixtures is readily explainable with the aid of a reasonable assumption about the cathodic discharge of complex anions containing aluminium. Such an assumption does not contradict any of the known experimental facts.

(c) *Dissociation in Slv–AlR_3 systems.* For such systems in the general case scheme (22) is the most probable. It is in accord with both the results of electrochemical investigations and with the thermochemical data. Obviously, this scheme remains true also for solutions of aluminium sesquihalides. In special cases when the solvent can form ions as a result of interaction with AlR_3§ here there can also be other variants. Thus interaction between RN≡NCl and $AlCl_3$ with the formation of $(RN{\equiv}N)^+.AlCl_4^-$ has been established[194]. This refers especially to solutions of AlX_3 in alkyl halides. The results of studies of isotopic exchange between EtBr* and $AlBr_3$ [215-217] and the isomerisation of hydrocarbons in the presence of RX and AlX_3 [218,219] show the formation of $R^+[AlX_4]^-$ complexes.

Good confirmation of the structure of complexes expressed by the formula $RAlX_4$ is given by the retardation or complete cessation of exchange of bromine between $AlBr_5$ and EtBr in solvents exhibiting strongly expressed donor properties. The rate of exchange changes thus: $Et_2O < PhNO_2 < MeNO_2 < MeCN$,[217] which should also be expected on the basis of series (16) and (17). It is interesting to note also that exchange of ethyl radicals is absent in mixtures of $AlEt_3$ and EtBr,[221-224] which is understandable, considering that the ethyl radical in EtBr has a positive charge and the orientation of EtBr in relation to $AlEt_3$ takes place according to the scheme $EtBr \rightarrow AlEt_3$ with formation of $Et^+.AlEt_3Br^-$. The possibility of appreciable dissociation of $RAlX_4$ into the ions R^+ and AlX_4^- was doubted[211] and it was suggested that possibly the matter is restricted by the strong polarisation of the R–X bond[218]. In support of the existence of such dissociation there is the slow decomposition of EtBr + $AlBr_3$ solutions with formation of alkenes and HBr;[50,51,77] from the measurements of the dielectric polarisation of these mixtures the conclusion was drawn that 3–4% of the EtBr molecules undergo dissociation[220]. Taking ΔH_1 for the reaction

$$EtBr(gas) \rightarrow Et^+(gas) + Br^-(gas),$$

as 183 kcal mole^{-1} after Streitwieser[225], we can evaluate ΔH for the reaction in an indifferent solvent:

$$EtBr + AlBr_3 \rightarrow Et^+ + AlBr_4^-, \qquad (25)$$

using the usual thermochemical cycle. We obtain

$$\Delta H = 117 + \Delta H_S \text{ kcal mole}^{-1}, \qquad (26)$$

where ΔH_S is the sum of the heats of solvation of the ions Et^+ and $AlBr_4^-$. Franklin[226] calculated the heat of solvation of Et^+ in H_2O and in MeOH as -54 and -59 kcal g-ion respectively. Taking into account that ΔH_S of $AlBr_4^-$ is of the same order, from Eqn. (26) it is evident that process (25) is by no means impossible. With increase in the length of the alkyl radical the quantity ΔH_1 decreases[225] and the formation of R^+ becomes more probable. Actually the decomposition of RBr + $AlBr_3$ solutions increases strongly on passing from ethyl to butyl[50,51]. However, concentrated EtBr–$AlBr_3$ solutions are completely stable and exhibit too high an electrical conductivity to suggest that they dissociate according to scheme (25). It seems that in this concentration region the bulk of ions is formed by scheme (22).

Jander and Kraffczyk[227] suggested, on the basis of the reaction between NaOEt and $AlBr_3$ in Et_2O, starting from the formation of NaBr and $Al(OEt)_3$, that in the solution there is a complex $Et^+[AlBr_3.OEt]^-$, reacting according to the scheme:

$$3NaOEt + Et^+[AlBr_3{\cdot}OEt]^- \rightarrow \underset{\downarrow}{3NaBr} + Al(OEt)_3 + Et_2O. \qquad (27)$$

Concerning the possibility of formation of this complex, all that has been said above regarding the EtBr–$AlBr_3$ system can be repeated. As for the reaction itself, it is by no means necessary to introduce any special hypotheses, as it can take place completely by the scheme:

$$3NaOEt + Et_2O{\cdot}AlBr_3 \rightarrow \underset{\downarrow}{3NaBr} + Al(OEt)_3 + Et_2O.$$

2. Ternary systems. Table 22 contains dissociation schemes proposed on the basis of the results of measurements of transport numbers and electrical conductivities, electrolysis data, and in some cases cryoscopic information. The possibility of the existence of Al^{3+} and AlX^{2+} ions was discussed above. The existence of ions of the type $(M_2AlX_4)^+$ is at least doubtful, since there are no evident reasons which might lead to their formation. On the contrary, all the remaining ionic formations are completely real and are precisely such as would be expected on the basis of the thermochemical and structural data. We note additionally that from the results of measurements of molar refraction in $MX–AlBr_3–C_6H_6$ solutions (M = Li, Na, K; X = Cl, Br), it was concluded[228] that the ions AlX_4^- and $Al_2X_7^-$ were formed.

From investigations of the spectra of solutions[71,229] and of the isotopic exchange of hydrogen between DX and aromatic hydrocarbons[120,230] it was concluded with a great deal of reliability that the complexes in the $HX–AlX_3–Ar$ systems have the structure $(ArH)^+(Al_2X_7)^-$ or $(ArH)^+AlX^-$. This conclusion agrees well with the electrolysis results (*cf.* p. 127).

§ Because of the conductivity of the pure solvents themselves it is necessary to assume that they are subject to self-dissociation. Reaction with AlR_3 can either facilitate this process, when at least one of the ions formed during self-dissociation will be present in mixtures with AlR_3, or give rise to the formation of other ions. Only the first case will be considered here.

TABLE 22. Results of investigating the composition of the ions in the ternary systems.

System	Cation	Anion	Reference
$KBr-AlBr_3-C_6H_6$	$[K_2AlBr_4]^+$	$Al_2Br_7^-$	207
$KBr-AlBr_3-PhNO_2$	K^+, $[Al.nPhNO_2]^{3+}$, $[AlBr.nPhNO_2]^{2+}$ at $KBr/AlBr_3 = 0.2-0.5$; K^+ at $KBr/AlBr_3 = 0.9$	$AlBr_4^-$	207
$NaBr-AlBr_3-EtBr$	Na^+, $[Al.nEtBr]^{3+}$, $[AlBr.nEtBr]^{2+}$ at $NaBr/AlBr_3 = 0.2-0.5$; Na^+ at $NaBr/AlBr_3 = 0.9$	$AlBr_4^-$ and $Al_2Br_7^-$	207
$IX-AlX_3-PbNO_2$ (X = Cl, Br)	I^+	AlX_4^-	111, 113
$EtPyBr-AlCl_3-C_6H_6$	$EtPy^+$	$[AlCl_3Br]^-$	143

Hence the main ionisation processes in the $MR-AlR_3-Slv$ ternary systems can be represented by the schemes:

1. For solvents which do not exhibit strong donor properties, in which AlR_3 is in the dimeric form:

$$MR + Al_2R_6 + nSlv \rightleftarrows M^+ + Al_2R_7^- + nSlv\,.$$

2. For solvents with strong donor properties:

$$2MR + [AlR_2 \cdot 2Slv]^+ + AlR_4^- + nSlv \rightleftarrows 2M^+ + 2AlR_4^- + (n+2)Slv.$$

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The generality of the properties of solutions of the aluminium compounds AlR_3 finds a natural explanation in the aluminium's having two free $3p$ levels. Such natural two-stage differences between particular solutions are linked both with the properties of R and consequently with a difference in the hybrid levels of AlR_3, and also with a difference in donor character of the solvents. The general position considered here can easily be applied both to solutions of Al homologues (for example, gallium [231]) and also to other solutions, for example, compounds of antimony [75], tin, etc.

We did not set ourselves the task of examining the influence of changes in concentration and the nature of the solvent on the properties of solutions of the complexes $MX.2AlX_3$ (*cf.*, for example, Refs. 232–235), considering that this could hardly add anything to the characteristics of the principal properties, although the investigations of such a nature are not without interest for the theory of solutions in media of low dielectric constant.

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ELECTRICALLY CONDUCTING NON-AQUEOUS SYSTEMS FORMED FROM NON-CONDUCTING COMPONENTS

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I. INTRODUCTION

The phenomenon of electrolytic dissociation in aqueous solution has been thoroughly studied, the number of papers on the electrical conductivity and the electrolytic dissociation of various electrolytes in aqueous solution having now reached several thousands. These papers are mainly concerned with extremely dilute solutions, the usual purpose of the work being to confirm the Debye–Hückel theory of electrolytic solutions. As a result, excessive attention has been paid to dilute aqueous solutions, whereas for a long time non-aqueous electrolyte solutions remained undeservedly outside the circle of interests of investigators. In this connection Lewis and Randall[1] correctly write: "Dilute solutions have played an extremely important part in the development of physical chemistry. Therefore exceptional, and perhaps even somewhat excessive, attention has been paid to very dilute solutions in both theoretical and experimental investigations".

Conant and Hall[2] in turn consider that "many chemical phenomena are obscured by our slavish devotion to water".

Thus comparatively little attention has been paid in the past to non-aqueous electrolyte solutions, although the study of electrolytic dissociation in non-aqueous media is not only of very great theoretical significance but also of great practical value in connection with the vigorous development of the electrochemical industry, especially the electrical synthesis of various substances from non-aqueous solvents.

It is sufficient to mention that in Brockman's monograph[3] alone, published as early as 1926, several hundreds of methods are described for preparing various organic compounds by anodic oxidation or cathodic reduction in organic solvents.

At the present time a vast literature has arisen on electrical synthesis in non-aqueous solvents[4-7].

As Antropov[5] correctly points out, however, in order that organic compounds can be obtained by electrical synthesis in non-aqueous solvents, the solutions employed must be good conductors; moreover, the mechanism of electrolytic dissociation of the substances forming the electrolyte in these non-aqueous solvents should be known. With most organic electrolytes, no data are available on their dissociation mechanism.

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Non-aqueous electrolyte solutions attracted the attention of individual workers a comparatively long time ago[8-20]. However, a more detailed study of such solutions was started only at the beginning of the present century.

In particular, Plotnikov concluded from an analysis of published data and his own results that the dielectric constant of the solvent is not the decisive factor in the dissociation of electrolytes. In support of this thesis he cited numerous data on the relation between electrical conductivity and the dielectric constant of the medium which contradict the Nernst–Thompson rule. Thus, for example, according to Plotnikov's results PBr_5 is non-conducting in water, but is a good conductor in bromine solution[21]. Cases are also known in which substances such as HCl and HI, which are strong electrolytes in water (D = 80), are not electrolytes in liquid HF, with the still higher dielectric constant of 84. On the other hand, many alcohols, carbohydrates, ketones, and other organic compounds, which are not electrolytes in water, behave as strong electrolytes in liquid HF.[22,23]

As a result of Plotnikov's work, it became generally recognised that in non-aqueous systems the dielectric constant of the medium is not the decisive factor (the "dissociating force") in the electrolytic dissociation of molecules.

Plotnikov's views were subsequently developed in numerous papers by Usanovich[24,25] who, following Konovalov[10], concluded, from an analysis of all the accumulated experimental results mainly on non-aqueous systems and from his own investigations, that the appearance of conduction in non-aqueous liquid systems produced from non-conducting components is due to the formation of electrically conducting complexes, not to the "dissociating power" of the solvent. This view was subsequently confirmed by other workers[26-28], and is now generally accepted, at least for systems formed from non-conducting components. The literature on this subject will be briefly surveyed below, the present Reviewer's researches on systems formed by organic isothiocyanates, thiocyanates, and various amines also being covered. More detailed attention will be paid to work on the mechanism of dissociation in the electrolytes formed. The present paper does not, of course, claim to cover fully the vast amount of experimental and theoretical work which has now been done on this problem.

II. ORGANIC ACID–AMINE SYSTEMS

Systems of this type were first studied by Konovalov[10]. On mixing pure acetic, propionic, and butyric acids with various amines (aniline, methylaniline, dimethylaniline, and *o*-toluidine) he obtained electrically conducting solutions, whose conductivity exceeded in individual cases 3×10^{-3} ohm^{-1} cm^{-1}. Separately, the components of these systems were practically non-conducting. Thus the conductivities of the acids and amines used did not exceed 10^{-6} ohm^{-1} cm^{-1}, so that the mixtures were better conductors than the components by a factor of 1000.

The conductivity isotherms of the binary systems formed from an acid and an amine passed through a maximum, which occurred at different ratios of the components in different systems (Fig. 1). Konovalov assumed that these maxima corresponded to a chemical compound formed when the components were mixed. A more detailed study of the acetic acid–aniline system, as well as the use of other methods of physicochemical analysis[29,30] has shown, however, that in the case of irrational systems† the maxima on the conductivity isotherms do not generally correspond in composition to the compounds which are formed in the system.

† The term "irrational system" is used in the Soviet literature apparently to denote a system in which chemical compounds are formed whose composition does not correspond to simple stoichiometric proportions of the components (Ed. of Translation).

Systems comprising an organic acid and an amine have formed the subject of many subsequent investigations [28-36], in all of which conductivity isotherms having a maximum have also been obtained. The absolute value of the conductivity is comparatively high, quite often exceeding that of 0.01 *N* potassium chloride solution at 18°. Such considerable conductivity in solutions formed from non-conducting components is undoubtedly due to the formation of a new compound which is an electrolyte.

In several cases conductance may not appear in the solutions when non-conducting components are mixed, as occurs very often with, for example, organic compounds (benzene and toluene, alcohols, etc.), but if the system does become conducting, an electrolyte must necessarily have been formed in it.

Apart from possible participation in the formation of chemical compounds, the role of non-conducting components consists mainly in the transfer of the compounds to the liquid state ("dissolution") if the latter are solid under the experimental conditions. This results in increased mobility of the ions.

Trifonov showed that, in the case of rational systems‡, the conductivity isotherm passes through a minimum at the composition of the compound which is formed [28,37], this minimum being caused by the high viscosity of the compound.

The view prevails in the literature that conductivity isotherms of rational systems formed from non-conducting components must necessarily have a minimum — if conducting compounds are formed — at the composition corresponding to such a compound. It appears to the Reviewer that this applies only to systems in which the viscosity of the compound is considerably greater than those of the components, as occurs, for example, in systems formed by mustard oil and piperidine [28]. When an electrolytic compound is formed in a system by interaction of the components, the conductivity isotherm should usually have one maximum, which does not always occur at the composition of the compound.

Investigation of Conducting Systems in a Third Component

Hölzl was the first to investigate the reaction of weak bases with organic acids in alcoholic solution [38].

Subsequently Izmailov demonstrated the advantage of investigating binary systems in a third, inert solvent [39,40]. He showed, in particular, that, when the components of a system are associated, physicochemical analysis of binary systems gives no positive indication of the presence or absence of interaction between them, whereas in a third component curves are obtained which may show not only interaction but also the composition of the compound which is formed. Any physical property (viscosity, refractive index, etc.) can be used for this purpose. More distinct maxima or inflections indicating compound formation appear on the conductivity isotherms for the ternary systems than on the diagrams of other properties, since in this case the conductivity is not appreciably affected by changes in the viscosity and the dielectric constant of the solutions.

The value of studying reaction between two components in a third, inert solvent has been shown also in a study [41] of the quinoline–acetic acid system. Although this system has been studied by various physicochemical methods, the number and the composition of the compounds formed between these components have not been finally established [42-44].

The above work and the present Reviewer's researches [41] show that two compounds, 1 : 1 and 2 : 1, are formed together in this system. Both are well revealed on the conductivity isotherms (20°, Fig. 2) obtained at equal concentrations of this system in a third component (methanol). These results again confirm the advantage of physicochemical investigation of the interaction of substances in a third component.

A study of solutions of amine–acetic acid binary systems in water [45] clarified the mechanism of the electrolytic dissociation of the resulting compounds and explained the origin of the high conductivity of some mixtures in these ternary systems. For example, results on electrolysis

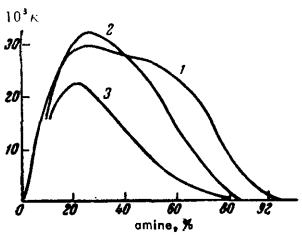


Fig. 1. Conductivity of binary systems formed by acetic acid with: 1) aniline; 2) methylaniline; 3) *o*-toluidine.

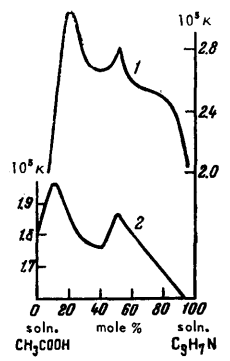


Fig. 2. Conductivity isotherms for the quinoline–acetic acid system in methanol: 1) 0.1 M solutions; 2) 0.01 M solutions.

‡ A "rational system" appears to be one in which a chemical compound of simple stoichiometric composition is formed (Ed. of Translation).

have suggested the following scheme for the dissociation of the complex compounds formed between acetic acid and aniline

$$C_6H_5NH_2 \cdot 2CH_3COOH \rightleftarrows C_6H_5NH_3^+ + CH_3COOHCH_3COO^-,$$

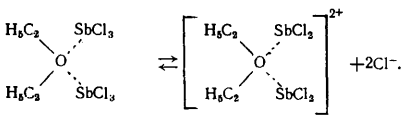
$$C_6H_5NH_2 \cdot CH_3COOH \rightleftarrows C_6H_5NH_3^+ + CH_3COO^-.$$

III. METAL HALIDE–ORGANIC COMPOUND SYSTEMS

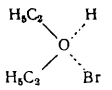
Systems formed from metal halides and organic compounds attracted the attention of investigators a long while ago. Thus as early as 1902, for example, Plotnikov[13] studied the conductivity of solutions of aluminium bromide in ethyl bromide, and concluded that the components interact to form a conducting complex.

The conductivity of the solutions exceeds many times those of the pure components at the same temperature. Subsequently Plotnikov and his pupils studied a series of systems formed by phosphorus and antimony halides in bromine and other non-aqueous media[46–50]. Complex formation was invariably observed, which, as is now known, is the reason for the high conductance of the solutions consisting of practically non-conducting components.

Systems formed from metal halides and organic compounds, principally ethers, have been studied in special detail by Usanovich and his coworkers[51–53]. Thus among others they studied[54] the antimony trichloride–diethyl ether system. From results on the conductivity and electrolysis of one such solution they conclude that the electrolyte here is a complex compound formed by interaction of the components



This compound resembles the oxonium compounds formed by the hydrogen halides with ether, discovered by Kablukov[55],



In aqueous medium it gives $[(C_2H_5)_2OH]^+$ ions, analogous to H_3O^+ ions.

Formation of such a compound in this system is confirmed by physicochemical data. In particular, the viscosity isotherm obtained by Kurnakov[56] has a maximum at 67 mole % of antimony trichloride. Usanovich and his coworkers have similarly studied other systems[57–60].

In the opinion of Usanovich[58] ethereal solutions are very convenient materials for study, since many substances are completely soluble in ethers with the formation of conducting solutions. This allows the examination of conductivity to be extended beyond a narrow concentration range, so that the system can be investigated as a whole with all possible proportions of the components.

Many workers have subsequently investigated systems formed by metal halides with esters. In 1936, for example, Kurnakov and Shternin studied the $SnBr_4$–$CH_3COOC_2H_5$ and $SnCl_4$–$CH_3COOC_2H_5$ systems by measuring the conductivity as well as the viscosity and melting point[61]. According to their results, compounds $SnX_4 \cdot 2CH_3COOC_2H_5$ are formed in these systems. The conductivity isotherm passes through two maxima and one minimum which occurs at the composition of the compound (67 mole % of the ester). This minimum is caused by the high viscosity of the compound. Hence if the effect of viscosity is eliminated, the solution containing 67 mole % of the ester will possess the maximum conductivity. This indicates that the compound is an electrolyte.

Several papers have been published on the mechanism of the electrolytic dissociation of this and other similar compounds. Thus the Reviewer was the first to try to elucidate the mechanism of electrolytic dissociation of the compound formed in the tin(IV) chloride–ethyl acetate system[62]. For this purpose the two solutions of maximum conductivity (containing 20 and 60 mole % of stannic chloride) were electrolysed in a vessel having separate cathode and anode compartments. On the basis of analyses of catholyte and anolyte, together with measurements of several of their physical properties, the following scheme was suggested for the dissociation of the compound formed

$$(SnCl_4 \cdot 2CH_3COOC_2H_5)_2 \rightleftarrows Sn(CH_3COOC_2H_5)_4Cl_2^{4+} + SnCl_6^{4-}. \quad (1)$$

Cryoscopic measurements of the molecular weight of the compound by Vol'nov[63] confirmed that its composition corresponds to the doubled formula $(SnCl_4 \cdot 2CH_3COOC_2H_5)_2$.

Subsequently Usanovich and his coworkers also studied the structure of several complexes, including $SnCl_4 \cdot 2CH_3COOC_2H_5$, formed by metal halides with esters and other organic compounds[64]. Mainly on the basis of the results of electrolysis, it is considered[64] that the only electrolytes in this and similar systems are the compounds $SnCl_4 \cdot 3RCOOR'$ and $SnCl_4 \cdot 4RCOOR'$, where R' is a proton or an aliphatic radical. The mechanism of the electrolytic dissociation of these compounds must be represented as follows

$$SnCl_4 \cdot 2RCOOR' + RCOOR \rightleftarrows [SnCl_4(RCOO)_2]R'^- + RCOOR'^+_2, \quad (2)$$

$$SnCl_4 \cdot 2RCOOR' + 2RCOOR' \rightleftarrows [SnCl_4(RCOO)_2]^{2-} + 2RCOOR'^+_2. \quad (3)$$

It is seen from this scheme that stannic chloride occurs only in the anion, while the organic molecules occur both in the anion and in the cation. In the Reviewer's scheme the organic molecules are present only in the cation.

The experimental results obtained by Usanovich and his coworkers[64] on the electrolysis of these complex compounds of stannic chloride and ethyl acetate agree in the main with the Reviewer's results[62], but, as is evident from a comparison of Eqns. (2) and (3) with (1), their scheme of electrolytic dissociation differs fundamentally from the latter's.

The weak point in the Usanovich scheme of dissociation seems to be, as these workers themselves point out[64], that no data have been published indicating the existence of 1 : 3 and 1 : 4 compounds of stannic chloride and ethyl acetate. Furthermore, the explanation of the formation of metallic tin and of tin(II) chloride at the cathode lacks adequate experimental basis, and is therefore unconvincing.

Recently Vol'nov has repeated the electrolysis of the series of complex compounds formed by $SnCl_4$, $SnBr_4$, and SnI_4 with various alcohols, organic acids, and esters, including ethyl acetate, and reached the conclusion that the

experimental results cannot be explained by the Usanovich scheme. He considers that the Reviewer's scheme involving electrolytic dissociation of the compound $SnCl_4 . 2CH_3COOC_2H_5$ is the most probable [63].

Reference must also be made to a series of interesting papers by Sumarokova and her coworkers on the reaction between stannic chloride and esters [65].

Other investigators have studied the interaction between metal halides and various classes of organic compounds. Gorenbein and his coworkers [66-68] have studied the conducting systems formed by $AlBr_3$, $AlCl_3$, and other metal halides in nitrobenzene, ethyl bromide, and other organic substances. They have shown in particular that aluminium bromide in nitrobenzene forms, according to conductivity data, three compounds, which are arranged in the following sequence of decreasing electrical conductivity [67]

$$(AlBr_3)_2 \cdot C_6H_5NO_2 > AlBr_3 \cdot 2C_6H_5NO_2 > AlBr_3 \cdot C_6H_5NO_2.$$

Usanovich and Sumarokova have studied systems formed by $SnBr_4$, $SnCl_4$, $SbCl_3$, and $AsCl_3$ with acetic acid and its chlorinated derivatives [70-73] and also with other acids [74-76]. These systems have attracted attention because $SnCl_4$ on Lewis and Randall's views, and $SbCl_3$ and $AsCl_3$ on the views of Usanovich, are aprotic acids. On the other hand, the acetic and chlorinated acetic acids which they used should act as oxonium bases towards these aprotic acids, and react with them by a kind of acid–base interaction. The isotherms for viscosity, conductivity, and other properties obtained by these workers support this hypothesis.

These investigators also studied several other electrically conducting systems formed by halides of metals in Groups IV and V of the Periodic System with various classes of organic compounds. For example, Usanovich [52] studied the conductivity of the systems formed by arsenic trichloride with nitrobenzene and with pyridine. The aim of this work was to prove that arsenic trichloride behaves towards nitrobenzene and pyridine as a substituted hydrochloric acid, somewhat as it behaves towards esters as an acid [52].

Interesting work has been done by Osipov and his coworkers on systems formed by the halides of titanium, zirconium, and germanium with esters and organic acids. They have made a detailed study, for example, of the conducting systems formed by the non-conducting components titanium tetrachloride with ethyl acetate [77], n-propyl acetate, and n-butyl acetate [78].

On the basis of physicochemical data (from diagrams of viscosity, heats of mixing, electrical conductivity, and other properties) they established that with esters titanium tetrachloride forms conducting complexes $TiCl_4 . E$ and $TiCl_4 . 2E$, where E represents a molecule of an ester of a monobasic acid. Electrolysis showed that these complex compounds dissociate according to the scheme [78]

$$(TiCl_4 . E)_2 \rightleftarrows [TiCl_2 . 2E] . TiCl_6 \rightleftarrows [TiCl_2 . 2E]^{2+} + TiCl_6^{2-},$$
$$(TiCl_4 . 2E)_2 \rightleftarrows [TiCl_2 . 4E] . TiCl_6 \rightleftarrows [TiCl_2 . 4E]^{2+} + TiCl_6^{2-}.$$

As the authors [79] themselves remark, this is analogous to the Reviewer's scheme of electrolytic dissociation for the complex compound $SnCl_4 . 2CH_3COOC_2H_5$. [62] Osipov and his coworkers have published many other papers on the reaction of zirconium halides with various organic compounds [80,81].

Recently Kudra and Ternovaya have studied the conducting systems formed by aluminium chloride with n-butyl ethyl ether and di-n-butyl ether [82].

IV. OTHER ELECTRICALLY CONDUCTING NON-AQUEOUS SYSTEMS FORMED FROM NON-CONDUCTING COMPONENTS

Among other electrically conducting non-aqueous systems, mention must first be made of those formed by the halogen compounds of iodine with various classes of organic compounds. Walden was one of the first to study the electrical conductivity of solutions of iodine monochloride, monobromide, and trichloride in liquid sulphur dioxide, sulphuryl chloride, and arsenic trichloride [83]. According to his results these solutions are comparatively weak electrolytes.

Later Bruns [84] and Bruner [85] measured the conductivity of iodine monochloride and trichloride in acetic acid and in nitrobenzene.

Further investigation of systems formed by iodine halides with organic substances showed the comparatively high conductivity of their solutions to be due to the formation of conducting complexes of the iodine halides with the solvent. For example, the complex compound formed in the highly conducting pyridine–iodine bromide system dissociates according to the scheme [86]

$$C_5H_5N . IBr \rightleftarrows [C_5H_5NI]Br \rightleftarrows [C_5H_5NI]^+ + Br^-,$$
$$C_5H_5NI_2 \rightleftarrows [C_5H_5NI]I \rightleftarrows [C_5H_5NI]^+ + I^-.$$ [87]

Systems consisting of iodine halides and acid amides also form highly conducting solutions [86]. The conductivity of the systems formed by iodine monochloride with acetamide and benzamide in nitrobenzene has also been studied [86].

Among conducting systems formed from non-conducting components, reference must be made to those formed by phosphorus pentachloride and pentabromide with the iodine halides, which have been well studied by Fialkov and his coworkers. It is interesting that, as Fialkov and Kuz'menko have shown [88], phosphorus trihalides do not yield compounds and do not form electrolytic systems with iodine. But PCl_5 and PBr_5 behave differently, oxidising iodine to its monochloride and monobromide, and thereby being reduced to PCl_3 and PBr_3 respectively. The iodine halides combine with still unchanged PX_5 molecules to form the complexes PCl_6I and PBr_6I, which are strong electrolytes, the maximum conductivity in these systems reaching 0.04 $ohm^{-1}\ cm^{-1}$.

The nature of the ions was established by studying their transport in nitrobenzene solutions of PCl_6I and PBr_6I. On the basis of the results, the following scheme of electrolytic dissociation is suggested

$$PCl_6I \rightleftarrows [PCl_4]^+ + ICl_2^-; \quad PBr_6I \rightleftarrows [PBr_4]^+ + IBr_2^-.$$

Like the phosphorus trihalides, those of antimony also interact neither with bromine nor with iodine, whereas antimony pentachloride reacts readily with iodine to form the electrically conducting complexes $SbCl_5 . 2ICl$ and $SbCl_5 . 3ICl$. [89]

At 45° systems formed by different aluminium halides with iodine halides arrange themselves in the following sequence according to their conductivity in the region of the maximum

$$ICl - AlCl_3 > ICl - AlBr_3 > IBr - AlBr_3$$ [90].

The acetic acid–acetyl chloride system, which was also investigated by Usanovich [91], forms conducting solutions. Its conductivity is due to the formation of the complex compound $(CH_3CO)_2OH.Cl$. Acid–base interaction

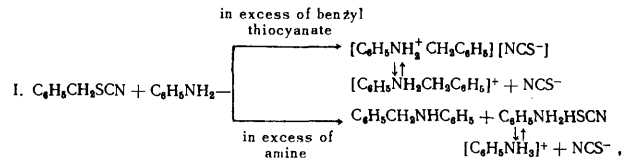
is assumed to take place, CH_3COCl being the acid, and CH_3COOH the base. From the results of electrolysis, the following scheme is suggested for dissociation of the conducting complex

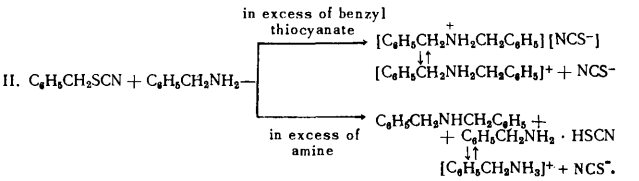
$$(CH_3CO)_2OH \cdot Cl \rightleftarrows (CH_3CO)_2OH^+ + Cl^-.$$

Finally, reference must be made to systems formed by organic thiocyanates and amines, which have recently been studied by Konovalova and Ust'-Kachkintsev [92]. They investigated the systems formed by ethyl thiocyanate with piperidine, aniline, dimethylaniline, and pyridine. In all these systems the solutions were good conductors, and the conductance increased on prolonged storage.

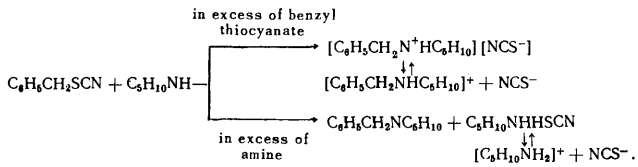
The Reviewer has also studied a series of systems [93] formed by benzyl thiocyanate with various amines (aniline, benzylamine, piperidine, and pyridine), which also are all good conductors. A high concentration of NCS^- ions can be detected in them by the usual qualitative tests. If this concentration is determined quantitatively (calorimetrically) as a function of composition, the resulting curve passes through a maximum at 50 mole %, which coincides with the maximum on the conductivity curve corrected for viscosity. Hence interaction of the components has yielded an electrolytic compound in which the anion is NCS^-. A detailed examination of these systems by various physicochemical methods and elementary analysis of the reaction products showed that two electrolytic compounds are formed from benzyl thiocyanate with primary and secondary amines depending on the proportions of the components.

It has been established [93] that the following reactions may occur on treatment of benzyl thiocyanate with aniline and with benzylamine





Benzyl thiocyanate reacts with piperidine according to the following scheme



Tertiary amines react with benzyl thiocyanate according to the same general scheme. In particular, pyridine forms one electrolytic compound, independently of the proportions of the components

$$C_6H_5CH_2SCN + C_5H_5N \rightleftarrows [C_6H_5\overset{+}{C}H_2NC_5H_5]\,[NCS^-] \rightleftarrows [C_6H_5CH_4NC_5H_5]^+ + NCS^-.$$

The saltlike compounds which are formed are responsible for the high electrical conductivity of the mixtures.

V. MUSTARD OIL–AMINE SYSTEMS

Zinin showed long ago [94] that, when mustard oil reacts with an amine, the corresponding substituted thiourea is obtained. Subsequently the interaction of mustard oils and various amines was more fully studied by Hofmann [95], Baxter [96], and other workers, who also found that substituted thioureas are formed. Kurnakov and his coworkers, who used various physicochemical methods to study a series of systems formed by mustard oils and amines, also confirmed that chemical reaction takes place with the formation of substituted thioureas in most cases of the mixing of mustard oils with primary and secondary amines [97].

Fig. 3 shows summary diagrams of the properties of the mustard oil–piperidine system taken from a paper by Trifonov [37]. These diagrams concern the formation of a thermally undissociated compound having the composition $C_5H_{10}NH.C_3H_5NCS$ *N*-allyl-*N'*-pentamethylenethiourea.

A considerable number of analogous systems formed by mustard oil and amines have been studied, among them being those formed by methylaniline [97,98], ethylaniline [28], etc.

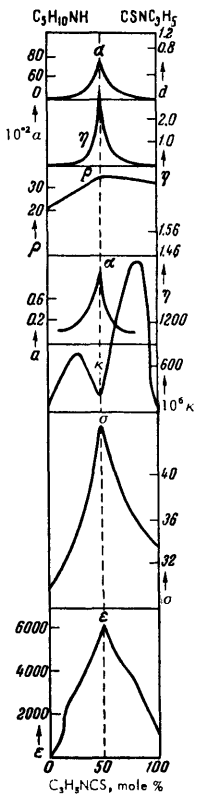


Fig. 3. Summary diagram of properties of mustard oil–piperidine system: η) viscosity; α) temperature coefficient of viscosity; P) polarisation; κ) conductivity; a) conductivity coefficient; σ) surface tension; ϵ) dielectric constant.

The conductivity isotherms of systems comprising a mustard oil and an amine show that the solutions possess considerable conductivity, which may sometimes exceed those of the components by factors of the order of 10^4.

Trifonov and Voskresenskaya studied the conductivity of many systems formed by mustard oil with various amines such as aniline, methylaniline, ethylaniline, *o*-toluidine, etc.[99]

Fig. 4 shows conductivity isotherms for systems comprising mustard oil and various primary and secondary amines. They all have two maxima and a minimum which occurs at 50 mole %, *i.e.* at the composition of the compound which is formed. As Trifonov[28] first established, such conductivity curves are characteristic of rational systems. If the effect of viscosity is eliminated, *i.e.* if the conductivity is corrected for viscosity and the result plotted against composition, a maximum is obtained in the place of the minimum. This indicates that in such systems the compound which is formed is actually the electrolyte.

If, however, it is supposed that a substituted thiourea alone is formed in the reaction of mustard oil with piperidine or other amine, in the present case *N*-allyl-*N'*-pentamethylenethiourea, it is difficult to imagine that this substance would be an electrolyte and decompose into ions. It is still less likely that either the mustard oil or the piperidine itself is an electrolyte. Trifonov calculated the equivalent conductance for piperidine in mustard oil as electrolyte, and for mustard oil in piperidine, and showed that in both cases the variation of equivalent conductance with dilution is anomalous[28]. In the opinion of Rabinovich[27] this indicates that the substances are not electrolytes.

We shall assume that in these systems the electrolyte is not the main product (substituted thiourea) formed by interaction of the components but a product of some side-reaction.

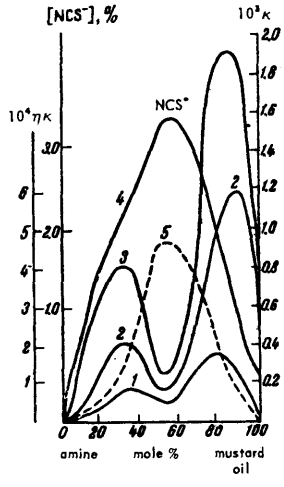


Fig. 4. Conductivity and corrected conductivity isotherms for systems formed by mustard oil with amines: 1) aniline; 2) anisidine; 3) piperidine; 4) [NCS⁻] in aniline system; 5) reduced conductivity in anisidine system.

A preliminary search for the ions into which this byproduct decomposes showed that the NCS^- ion can be detected in solution by qualitative tests on many systems formed by a mustard oil and an amine. This gave grounds for assuming that formation of the substituted thiourea was accompanied by that of a second compound, containing NCS^- as anion.

Further work by the Reviewer completely supported this hypothesis. It was therefore of interest to study in detail a series of such systems in order to establish the chemical nature of the compounds responsible for the comparatively high conductivity of these systems, and also to study the mechanism of electrolytic dissociation and measure the dissociation constants of the compounds in various solvents.

Systems formed by mustard oil with tertiary amines (pyridine, quinoline, dimethylaniline, etc.) are of especial interest. According to published data, tertiary amines do not interact with mustard oil. However, Voskresenskaya established that the conductance isotherm has a well-defined maximum, the conductivity of individual solutions exceeding those of the components by factors of the order of 10^4.

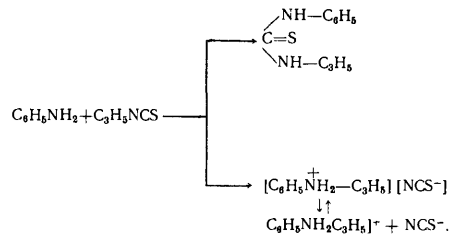
If no chemical reaction takes place between the components, the question arises as to what is the electrolyte in the system. It is quite improbable that the components of the mixtures would conduct the current[100]. In searching for the ions responsible for conduction in such solutions, the Reviewer also has detected the NCS^- ion. As will be shown below, in these systems, too, reaction of mustard oil with tertiary amines yields a saltlike compound having NCS^- as anion.

1. Mustard Oil–Primary Amine Systems

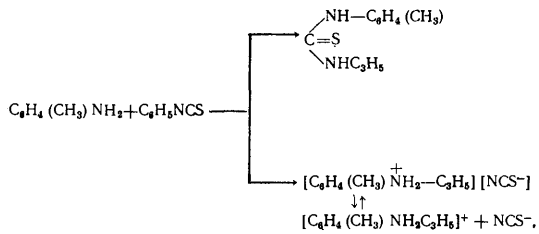
The mustard oil–aniline system has been studied by many workers[28,97]. The conductivity isotherms for 100° and 125° have two maxima and one minimum, which occurs at the composition of the compound (see Fig. 4). This is not because mixtures close to 1 : 1 in composition contain a lower concentration of electrolyte, but because these solutions are very viscous[97]. Indeed, if the effect of viscosity is eliminated — by measuring the conductivity in a third component (ethanol) or calculating the conductivity corrected for viscosity — the minimum is replaced by a maximum (see broken curve in Fig. 4). The conductivity of individual solutions in the system reaches 0.0043 $ohm^{-1} \times cm^{-1}$. The occurrence of such a high conductivity cannot be explained on the assumption that allylphenylthiourea is the sole product of interaction of the mustard oil with the aniline, since it is difficult to accept that this substance would undergo electrolytic dissociation. It therefore appears to the Reviewer that, in this and analogous systems, the electrolyte is not the substituted thiourea but a compound formed by some side-reaction. The NCS^- ion has been detected in all solutions in this system by the usual analytical methods (reaction with $FeCl_3$, etc.)[100]. It was therefore decided to measure the NCS^- concentration (by a colorimetric method) as a function of composition. The resulting curve (Fig. 4, curve *4*) runs roughly parallel to the curve for the corrected conductivity of this system. This indicates that the electrolyte is a compound having NCS^- as anion.

The Reviewer has been able by extraction with aqueous ammonia to isolate crystalline NH_4SCN from this system, which provides incontrovertible proof of the presence of NCS^- ions. From these and several other results it has

been shown that the aniline–mustard oil system contains, together with the substituted thiourea (a non-electrolyte) allylanilinium thiocyanate, which is the electrolyte responsible for the high conductance of the solutions:

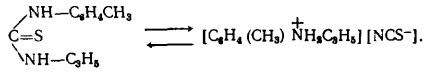


Reaction of *o*-toluidine with mustard oil also yields a substituted thiourea[94], which, according to the results of the Reviewer[100], is practically non-conducting ($\kappa_{100°} = 2 \times \times 10^{-6}$ ohm^{-1} cm^{-1}). However, as Trifonov[28] showed long ago, solutions of this system possess considerable conductivity ($\kappa_{max} = 10^{-3}$ ohm^{-1} cm^{-1}). The Reviewer has established that, in this system too, the comparatively high conductivity is caused by the formation, together with the main reaction product (allyl-*o*-tolylthiourea) when the components are mixed, the electrolyte allyl-*o*-toluidinium thiocyanate



The Reviewer has also proved that this electrolytic compound is formed in this and similar systems by studying ionic transport in a special apparatus[100]. As a result of electrolysis, NCS^- ions accumulate in the anode compartment, and $[C_6H_4(CH_3)NH_2C_3H_5]^+$ ions (in the form of the hydroxide) in the cathode compartment.

The concentration of this electrolytic compound in the system increases both on prolonged storage and especially on heating, as the Reviewer's experiments have shown. It was found that part of the substituted thiourea was converted, on being heated, into the allylammonium thiocyanate according to the equation[100]



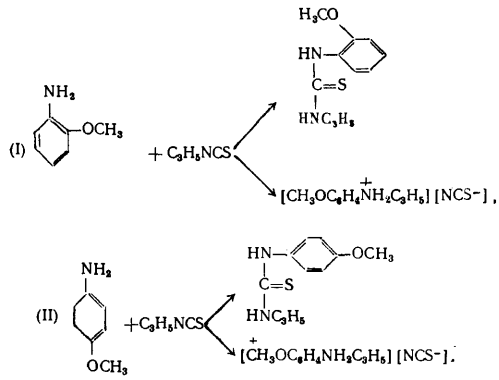
This agrees well with published information on the possibility of such changes[101,102].

Systems formed by mustard oil with other primary amines are not found in the literature, if we do not count the mustard oil–ethylenediamine system studied by Dianov and Trifonov[103], the conductivity of which has not been investigated, obviously because the system is not electrically conducting. With the aim of finding new conducting systems formed by mustard oil with other primary amines, the Reviewer has studied the reaction of the former with *o*- and *p*-anisidines, benzylamine, and also several aliphatic primary amines (methylamine, ethylamine, and isopropylamine).

Investigation of the systems containing *o*- and *p*-anisidines by physicochemical methods, including conductance[104], showed that mixtures of these systems are also good conductors ($\kappa^{60°}_{max} = 0.0012$ ohm^{-1} cm^{-1}) and contain the NCS^- ion.

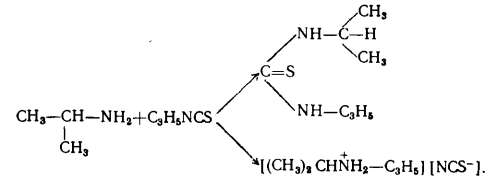
The conductivity isotherms also have two maxima and one minimum, which occurs at equimolecular proportions of the components, *i.e.* at the composition of the compound which is formed in the system (Fig. 4). Curves representing variation of the corrected conductivity and the NCS^- concentration with composition have well-defined maxima at 50 mole % of the components, which indicates that the compound formed in the system is the electrolyte.

On the basis of the property diagrams and several other results the Reviewer has shown that, in these systems too, two simultaneous reactions take place, with formation of a non-electrolytic compound (a substituted thiourea) and an electrolytic compound, according to the schemes



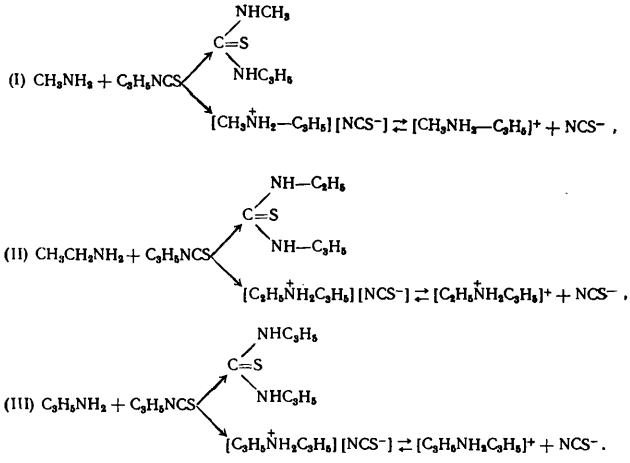
In several cases the Reviewer has been able to isolate this electrolytic compound and subject it to electrolysis. Analysis of catholyte and anolyte showed that NCS^- migrates to the anode, and the complex ion $[R'NH_2R]^+$ to the cathode. This confirms the above scheme of electrolytic dissociation of the compounds.

Study of the reaction of mustard oil with aliphatic amines was of considerable interest, since they are more strongly basic than are aromatic amines. No information on systems comprising mustard oil and aliphatic amines were found in the literature, and the Reviewer has therefore made a detailed physicochemical examination (by determining crystallisation temperature, density, viscosity, electrical conductivity) of the mustard oil–isopropylamine system[105]. The curves for all these properties have singular points at the composition of the 1 : 1 compound, a crystalline substance being formed. Elementary analysis showed it to be a substituted thiourea, *i.e.* allylisopropylthiourea. However, the high conductivity of this system ($\kappa^{50°}_{max} = 0.0016$ ohm^{-1} $\times$ $\times$ cm^{-1}), as well as the considerable concentration of NCS^- ions in these mixtures, indicates the simultaneous formation of allylisopropylammonium thiocyanate, according to the scheme



When this system is heated, both the conductance and the NCS^- concentration increase rapidly, owing to partial conversion of the substituted thiourea into the thiocyanate at the high temperature.

The Reviewer has also studied the interaction of mustard oil with methylamine, ethylamine, and allylamine[106]. Here, too, simultaneous reactions take place, with formation of a substituted thiourea (non-electrolyte) and of an allylammonium thiocyanate according to the scheme

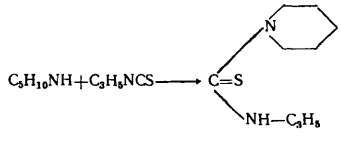


Summarising the reactions between mustard oil and primary amines, we can conclude that they form mainly non-conducting crystalline substances — substituted thioureas — but that a simultaneous side-reaction results in the formation of an allylammonium thiocyanate, which is an electrolyte and responsible for the high electrical conductivity of these systems. In individual cases the content of this electrolytic compound is 3% (in the mustard oil–isopropylamine system), increasing after heating to 24%.

Thus the Reviewer has succeeded in showing that conduction in these systems is not due to the principal reaction product (a substituted thiourea), as had previously been assumed[28,29], but to an electrolytic compound formed by a side-reaction.

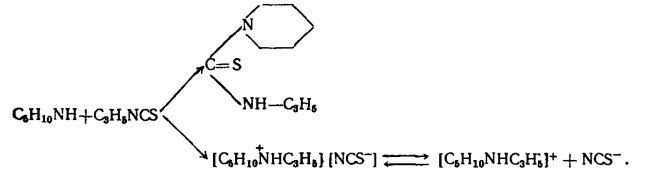
2. Mustard Oil–Secondary Amine Systems

Among systems formed with secondary amines, the mustard oil–piperidine system has been very thoroughly studied. It was assumed on the basis of viscosity, density, refractive index, and other measurements (see Fig. 3) that the compounds interact completely to form allylpentamethylenethiourea



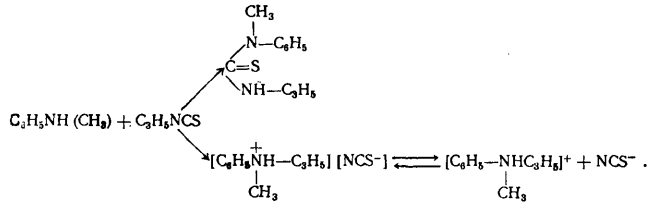
However, as measurements by Trifonov and his coworkers[28,107] showed, mixtures in this system possess comparatively high conductivity ($\kappa_{max}^{25°} = 0.0014$ ohm^{-1} cm^{-1}), and its conductivity isotherm has the form typical of rational systems, *i.e.* with one minimum and two maxima, the minimum occurring at the composition of the compound. Trifonov showed that neither component is an electrolyte[28]. He therefore assumed that allylpentamethylenethiourea was the electrolyte. It seems to the Reviewer highly improbable that a substituted thiourea would break down into ions, especially as Trifonov gave no experimental evidence.

As early as 1953 the Reviewer was able to show, on the basis of experimental results[108], that here, too, a parallel reaction takes place, with simultaneous formation of a substituted thiourea and allylpiperidinium thiocyanate, the latter of which is the electrolyte and is responsible for the high conductivity of the system



Later the Reviewer again studied this system, by electrolysing the electrolytic compound and also measuring the e.m.f. of the voltaic cell comprising glass and calomel electrodes[109]. The resulting e.m.f.–composition curve for the system resembles a potentiometric titration curve for a strong acid with a strong base, indicating the acid–base character of the interaction between the components with formation of a salt-like compound. This is consistent with the above scheme of interaction between the components with formation of allylpiperidinium thiocyanate.

The system formed by mustard oil and methylaniline has also been well studied by many physicochemical methods[28,97,98]. The isotherms of all properties are singular in character, and indicate the formation of a substituted thiourea, allylmethylphenylthiourea. Thus Voskresenskaya found[99] that the system possesses considerable conductivity. The Reviewer's investigations of this system[110] showed that here, too, the main reaction product (allylmethylphenylthiourea) is accompanied by allylmethylanilinium thiocyanate, dissociation of the latter being responsible for the conductivity of mixtures in the system



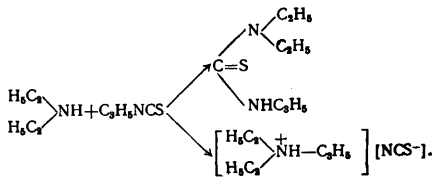
The curve obtained by the Reviewer for variation of the concentration of NCS^- ions with the composition of the mixtures show a parallel variation to the corrected conductivity isotherm, which indicates that the electrolyte is in fact allylmethylanilinium thiocyanate.

The viscosity, density[111], and surface tension[28] of the mustard oil–ethylaniline system have been studied. The diagrams of these properties have a singular maximum and indicate the formation of allylethylphenylthiourea. Trifonov and Cherbov[34], as well as Voskresenskaya[99], measured the conductivity of this system, and also obtained a "double-humped" isotherm, the maximum conductivity of individual solutions reaching 0.0013 ohm^{-1} cm^{-1}. The high conductivity was attributed to the reaction product, allylethylphenylthiourea. The Reviewer's investigations of this system

showed that the electrically conducting compound is not the substituted thiourea but allylethylanilinium thiocyanate $[C_6H_5\overset{+}{N}H(C_2H_5)C_3H_5][NCS^-]$, which is formed in considerable quantities (up to 25%), especially on heating.

It was of interest to investigate the nature of the reaction of mustard oil with aliphatic secondary amines, since the latter are stronger bases than the corresponding aromatic amines. No data on such systems were found in the literature, and therefore the Reviewer [112] has studied the melting point, viscosity, and density of the mustard oil–diethylamine system. The diagrams of all the properties indicate formation of a 1 : 1 compound, confirmed by the precipitation of crystals. The measurements showed that this system, too, is a good conductor ($\kappa^{40^\circ}_{max} = 0.0015\ ohm^{-1} \times cm^{-1}$).

All solutions in this system give an intense reaction for NCS^-, the concentration of which varies with composition in the same sense as the isotherm for the reduced conductivity (corrected for viscosity). From these and other experimental results the Reviewer has shown that simultaneous reactions take place in this system, too, with the formation of a substituted thiourea and of allyldiethylammonium thiocyanate (an electrolyte)



3. Mustard Oil–Tertiary Amine Systems

As already stated above, there are indications that tertiary amines do not react with mustard oil. Thus Kurnakov studied viscosity and density in the mustard oil–pyridine system [97], and obtained smooth isotherms for the former, slightly concave to the concentration axis. Such curves are known to be obtained in the absence of interaction between the components of a system. A similar conclusion was reached by Fialkov and Muzyka [113] from a cryoscopic study of this system, and also by Sheka and Karlysheva [114], who investigated dielectric constant and polarisation.

According to Voskresenskaya [99], however, this system possesses high electrical conductivity, which increases on storage. The conductivity isotherm for the mustard oil–pyridine system after standing for a month (Fig. 5) [99] shows that the maximum conductivity reaches 0.0016 $ohm^{-1}\ cm^{-1}$ at 50° and occurs at about 50 mole % of the components. This seems to the Reviewer to contradict the results of physicochemical analysis, since it is impossible to explain the occurrence of such a high conductivity if it is accepted that the components do not interact. There are no grounds for assuming that either of the components is an electrolyte. The Reviewer therefore assumed that in this case the mustard oil nevertheless reacts with pyridine to form a conducting complex. Obviously, the fact is merely that at room temperature this reaction takes place to such a slight extent that it cannot be detected by the viscosity method or other methods of physicochemical analysis owing to their relative insensitivity.

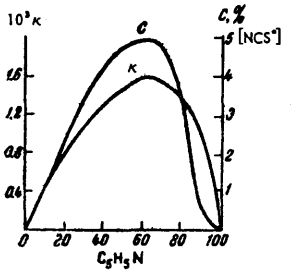


Fig. 5. Conductivity (κ) and NCS^- concentration in the mustard oil–pyridine system.

Electrical conductivity is known to be one of the most sensitive properties, and therefore its isotherm shows a clearly defined maximum. Further investigations by the Reviewer on the mustard oil–pyridine system [115] showed also that mixtures contain the NCS^- ion (see NCS^- curve in Fig. 5), the concentration of these ions increasing very rapidly and exceeding 60% on heating, while the viscosity isotherm shows a sharp maximum. All these and other experimental results undoubtedly indicate that a Menshutkin type of reaction is taking place here between the components [116]

$$C_5H_5N + C_6H_5NCS = [C_5H_5\overset{+}{N}—C_6H_5][NCS^-] \rightleftharpoons [C_5H_5NC_6H_5]^+ + NCS^-.$$

The saltlike compound which is obtained is known to be a strong electrolyte and is responsible for the high conductance. This reaction is analogous to the well-known reaction between methyl iodide and pyridine

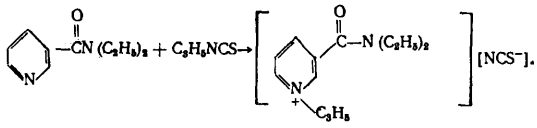
$$C_5H_5N + CH_3I = [C_5H_5\overset{+}{N}CH_3]I^-.$$

The Reviewer has shown [117] analogously that, in the mustard oil–quinoline system at room temperature, interaction between the components is too feeble to be detected on the viscosity and density diagrams. However, here, too, the conductivity isotherm passes through a maximum, approximately at 50 mole % of the components, which indicates that very weak interaction between the components is taking place at this temperature. On heating, this reaction becomes very vigorous, and then the viscosity and density isotherms show well-defined maxima at the same composition. All these and other results show that here, too, an electrically conducting saltlike compound is formed, as a result of interaction between mustard oil and quinoline

$$C_9H_7N + C_3H_5NCS = [C_9H_7\overset{+}{N}C_3H_5][NCS^-] \rightleftharpoons [C_9H_7NC_3H_5]^+ + NCS^-.$$

Subsequently the Reviewer also studied the mustard oil–diethylnicotinamide system, the second component in which is also a cyclic tertiary amine. The viscosity and density isotherms obtained curve smoothly from one component to the other without passing through any extremal points, which indicates that interaction is either absent or very weak. However, the mixtures conduct an electric current, although only slightly, and give a positive reaction for the NCS^- ion. After heating, the viscosity and density isotherms show well-defined maxima, while the conductivity and the NCS^-

concentration in the mixtures increase markedly. The Reviewer has shown that, in this system, too, an electrolytic complex compound is formed by the reaction [118]

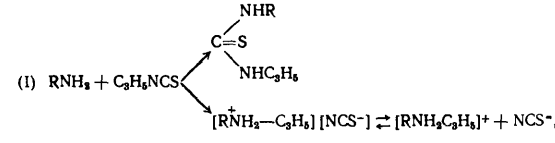


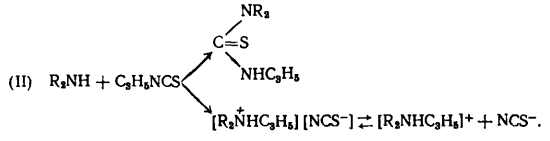
Finally, the Reviewer has also studied one system comprising mustard oil and triethylamine, which is an aliphatic tertiary amine. The viscosity and conductivity isotherms show that the components react feebly at room temperature (more strongly than in the case of cyclic tertiary amines), but the reaction becomes vigorous on heating, with formation of a conducting compound

$$(C_2H_5)_3N + C_3H_5NCS = [(C_2H_5)_3\overset{+}{N}C_3H_5][NCS^-] \rightleftarrows [(C_2H_5)_3NC_3H_5]^+ + NCS^-.$$

Thus the results of these investigations disprove the statement by several authors that tertiary amines do not react with mustard oil. According to these data, interaction takes place even at room temperature, with the formation of electrically conducting solutions.

Summarising, we can state that reaction of mustard oil with primary and secondary amines yields, together with substituted thioureas (non-electrolytes), allylammonium thiocyanates (electrolytes) according to the following general scheme





With tertiary amines only the one, electrolytic compound is formed, according to the general scheme

$$R_3N + C_3H_5NCS = [R_3\overset{+}{N}C_3H_5][NCS^-] \rightleftarrows [R_3NC_3H_5]^+ + NCS^-.$$

The Reviewer has confirmed this by a spectrophotometric method [119].

4. Dissociation Constants of the Electrolytic Compounds

Most of these saltlike compounds were isolated [120], and their electrolytic dissociation constants measured by the conductivity method in various solvents (water, methanol, and ethanol). The results are summarised in the accompanying Table, in which all the saltlike complex compounds obtained by the Reviewer are arranged in order of increasing basic dissociation constant of the amine (third column).

The dielectric constants of the solvents used differ considerably among themselves, which makes it possible to trace their effect on the dissociation constants of the electrolytes. From the data in the Table it is seen that:

1. The dissociation constants of the electrolytes in water decrease with decrease in the dissociation constant of the amine which they contain. This generalisation does not apply when the solvent is methanol or ethanol.
2. The dissociation constants of the salts increase with decrease in the dielectric constant of the medium, whereas the equivalent conductance at infinite dilution increases with increase in the dielectric constant.

These results are not consistent with the Nernst–Thompson rule, according to which the dissociation power of a solvent should increase with increase in the dielectric constant of the medium.

It seems that this is associated with hydrolysis of these substituted ammonium thiocyanates, resulting in the appearance of more mobile ions. At very high dilutions in aqueous

TABLE.

Formula of thiocyanate	Name of cation	Dissociation constant of amine	Water, $D = 81$		Methanol, $D = 35$		Ethanol, $D = 25.4$	
			λ_∞	$10^4 K_{diss}$	λ_∞	$10^4 K_{diss}$	λ_∞	$10^4 K_{diss}$
$[C_5H_{10}\overset{+}{N}HC_3H_5][NCS^-]$	allylpiperidinium	1.6×10^{-3}	85	3.8	94	33.1	38	50.1
$[(CH_3)_3\overset{+}{N}C_3H_5][NCS^-]$	allyltriethylammonium	5.6×10^{-4}	225	2.0	180	11.0	65	20.0
$[C_5H_5\overset{+}{N}C_3H_5][NCS^-]$	allylpyridinium	1.7×10^{-9}	232	1.51	127	3.16	60	7.94
$[C_6H_5\overset{+}{N}(C_2H_5)HC_3H_5][NCS^-]$	allylethylanilinium	1.3×10^{-9}	220	1.3	110	5.62	52	10.4
$[C_9H_7\overset{+}{N}C_3H_5][NCS^-]$	allylquinolinium	6.3×10^{-10}	228	0.89	192	2.88	66	11.2
$[C_6H_5\overset{+}{N}(CH_3)HC_3H_5][NCS^-]$	allylmethylanilinium	5×10^{-10}	220	0.74	140	4.36	44.5	10.0
$[CH_3OC_6H_4\overset{+}{N}H_2C_3H_5][NCS^-]$	allyl-*o*-anisidinium	2.5×10^{-10}	245	0.39	130	7.08	48	13.5
$[(C_2H_5)_2NCOC_5H_4\overset{+}{N}C_3H_5][NCS^-]$	1-allyl-3-diethylcarbamoylpyridinium	–	255	0.31	184	1.90	58	13.8

medium it is possible that these salts are completely hydrolysed with the formation of hydrogen ions, which possess the highest mobility, according to the scheme

$$[R\overset{+}{N}H_3{-}C_5H_5][NCS^-] + H_2O \rightleftharpoons [R\overset{+}{N}H_2C_5H_5][OH^-] + HSCN$$
$$+H_2O \downarrow\uparrow$$
$$H_3^+O + NCS^-$$

This hypothesis is supported by the fact that the equivalent conductance of these salts at infinite dilution in aqueous solutions reaches values of 220–225 ohm^{-1} cm^2.

Similar phenomena were observed also by Burmistrova [121] in a study of the electrolytic dissociation of quaternary ammonium salts in methanol and ethanol. She found that on dilution the equivalent conductance of such salts at first increases steadily though not greatly, but when a concentration of about 10^{-4} M is reached, a rapid rise in equivalent conductance begins with most salts. She observed a similar phenomenon in aqueous solutions of quaternary ammonium salts too. She regards the great increase in equivalent conductance at high dilutions as being due to interaction between solvent and electrolyte, *i.e.* to solvolysis.

According to Burmistrova's results, solvolysis is greater in methanol than in ethanol. Values obtained by the Reviewer for the equivalent conductance at infinite dilution of the salts which he studied were also considerably greater in methanol than in ethanol. This indicates that these salts, too, undergo stronger solvolysis in the former solvent.

Burmistrova also assumes that a proton can be split off more readily from an allyl than from a benzyl group. The salts examined by the Reviewer contain an allyl group, which makes his explanation involving hydrolysis (solvolysis) of the salts probable.

Of all the salts studied by the Reviewer, only allylpiperidinium thiocyanate has a relatively low value of λ_∞ in all solvents, especially water. This is probably because, owing to its stability, this compound is hydrolysed less or not at all in water. This agrees with Burmistrova's experimental results [121], showing that λ_∞ for solutions of NaBr in ethanol does not increase so rapidly as for salts of quaternary ammonium bases even at very high dilutions.

It is possible that the presence of such a strong base as piperidine in a salt confers stability on the latter and protects it from hydrolysis (solvolysis).

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There is no doubt that study of the electrical conductivity of non-aqueous solutions will continue in the future to make a great contribution to the formulation of a single, generally applicable theory of electrically conducting solutions. Attempts have already been made to work out such a theory. An example is provided by Izmailov's theory of solutions [122-124], which takes into account the properties of non-aqueous conducting solutions.

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MODERN VIEWS ON THE PLASTICISING OF POLYMERS

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1. INTRODUCTION

There have been various fundamental changes in views on the structure of linear polymers and the nature of plasticising which have not found their way into the reviews on the subject (see *e.g.* Tager[1]). We thought it desirable to collect the main facts about the plasticising of polymers by low-molecular-weight plasticisers without considering the questions of chemical and mechanical plasticising and the plasticising of polymers by high-molecular substances.

Polymers without additives are comparatively rarely used in technology because of their considerable brittleness, their tendency to crack during storage and use, the difficulty of forming them into articles, and various other deficiencies; the polymers are therefore modified, *i.e.* their properties are changed (improved).

One of the most important methods of modifying the properties of linear polymers is to plasticise them with low-molecular-weight substances. This type of plasticising can be considered as the combination of the polymers with certain low-molecular-weight substances of a definite chemical structure to form, because of steric effects and the altered energy relationships, polymeric materials which are usually more plastic and more elastic. The substances producing this effect are known as plasticisers.

For a long period the problem of plasticising has been solved purely empirically. A theoretical founding of this effect became possible only after the basic kinetic features of the behaviour of polymers had become evident, and after the discovery of the relaxation mechanism of the deformation of polymeric materials and the introduction of the concepts of the macromolecular and then of the globular-packet structure of high-molecular-weight compounds.

It has been shown[2] that the extent of highly elastic deformation has a clearly expressed relaxation (retardation) character, *i.e.* it depends on the period over which deformational stresses act on the polymer. Brittleness appears in polymers when the increase in stress in specimens subjected to deforming forces is not accompanied by macromolecular rearrangements leading to stress-relaxation[3]. Hence it is concluded that the brittleness of polymers can be reduced by the introduction of plasticisers, since in their presence the rates of relaxation processes are increased and the growth of cracks is stopped or greatly reduced.

The mechanical properties of polymeric materials have been determined as a function of the period over which external forces act upon them[4]; the strength of polymers and similar materials depends greatly on the duration of deforming stresses on the specimen, and all polymeric materials have such a strength *vs.* time relationship[5-7].

X-Ray and electron diffraction of amorphous polymers[8-10] have clarified the structure of such substances and allowed the orientated state of the chains to be considered as an enforced and unstable state of the polymeric system. Similar conclusions were reached from an investigation of the differential heats of sorption of polymeric materials[11].

The change in views of the structure of polymers has enabled knowledge of their behaviour on deformation to be expanded. In linear polymers under certain conditions there is movement of the chains as a whole, causing the plastic properties (flow) of polymers, and movement of individual segments of the chains, producing flexibility and elasticity of the polymeric material[12]. The flexibility of the macromolecular chains is in its turn determined by the potential barrier, *i.e.* the energy required to pass from one conformation to another. The potential barrier depends on the chemical nature and structure of the chains producing the intramolecular and intermolecular interactions, and on the temperature and various other factors. Depending on the temperature, polymers can exist in three main physical states[13-15]: vitreous, highly elastic, and viscous liquid; the length and flexibility of the macromolecules play a significant part in these transformations. Further studies led[16] to a theory of the mechanical properties of amorphous linear polymers and to two mechanisms for

vitrification, based on (1) the increase of viscosity with fall in temperature, and (2) the sharp increase of the rigidity of chain molecules on cooling. Two different plasticising mechanisms must correspond to the two vitrification mechanisms.

Extensive electron microscopic studies led[17] to the globular-packet theory of the structure of linear polymers.

A consequence of the changes enumerated above in views on the structure and properties of linear polymers has been a more correct evaluation of the nature and laws of the plasticising of polymers by low-molecular-weight substances.

2. HISTORICAL

(a) The Plasticising of Amorphous Polymers

Plasticising has long been used technologically to improve certain properties of polymers. More than 100 years ago castor oil[18] and camphor[19] were employed to plasticise cellulose nitrate, and at the beginning of the 20th century tricresyl phosphate began to be used for the same purpose. Paraffin, tars, waxes, and bitumens have been used as plasticisers (softeners).

Attempts to explain the plasticising of specific polymers were made in the nineteen-twenties and -thirties by Obrist[21] who proposed the now discarded colloidal theory of plasticising, and by others[22-24].

Ueberreiter[11] introduced the term "internal plasticising of polymers" by which he meant the penetration of plasticiser molecules between the macromolecular chains of the polymer, causing them to separate and weakening the interaction between them.

The plasticising of polymers by low-molecular-weight substances can, as we have said[25], be called "physical plasticising", since the new plasticised polymeric system is produced solely as the result of various physical bonding forces.

Several workers have considered plasticising as the blending of liquids[30]. It has been said[26-31] that the plasticiser molecules diffusing into the polymer enter into a definite energetic interaction with certain groups of the macromolecular chains, forming with them molecular sorption compounds of a certain type. The particular action of plasticisers on polymers is determined, according to Kirkpatrick[32], by the presence in polymer and plasticiser of groups which can interact with each other, by their most favourable mutual disposition, by the shape of the plasticiser molecules, and by purely geometrical factors.

The phase equilibrium in colloidal systems of the polymer–plasticiser type, the equilibrium conditions in such systems, and the change of the mechanical properties of the products have been studied as functions of temperature and amount of plasticiser[33-35]. The equilibrium diagram has been used to indicate the range of compatibility of the plasticiser with the polymer[34]; the compatibility of plasticiser and polymer was shown to depend on the position of the curve depicting the separation of the system into two phases. The properties of the polymer–plasticiser system have been more fully described by using the temperature *vs.* composition diagram on which the isoviscous solution curves are plotted as well as the phase equilibrium curve of the components[35]. It was assumed that a given plasticiser can affect the plasticity and elasticity of the polymer, depending on the amount of plasticiser added to the polymer system.

In a polar polymer a typical plasticiser is not randomly distributed[36], since it interacts mainly with the polar groups of the polymer. Under such conditions the plasticiser can block the force field of these polar groups, weakening the interaction between neighbouring chains, *i.e.*, the polymer becomes, as it were, less polar as the result of the plasticising.

Plasticisers have been divided[37-39] into actual plasticisers, which only increase plasticity (*e.g.* dimethyl phthalate), and the so-called elasticisers (*e.g.* dibutyl phthalate) which at a definite content also increase the elasticity of the polymer.

The thermodynamic theory of polymer solutions[40] has been used to attempt a quantitative interpretation of the mutual solubility of polymers and plasticisers[41]. The interaction in the system depends very greatly on the vapour pressure of the plasticiser and the temperature and is independent of the type of plasticiser[42].

A mainly new and thorough quantitative investigation of the plasticising of polar and non-polar polymers was carried out in the early nineteen-forties by Zhurkov[43-45], who formulated the rule of "mole fractions", which states that with polar polymers the plasticising effect depends on the mole fractions of polar plasticisers introduced, but is independent of their size, chemical nature and structure. Similar conclusions were reached by Fuoss and coworkers[46] when studying the plasticising of poly(vinyl chloride) by various low-molecular-weight substances, but the rule was not obeyed in the case of poly(vinyl chloride) copolymers.

Later Zhurkov and Levin showed[47] that reaction between the polar groups of polymer and plasticiser is indicated by the appearance in the spectrum of poly(methyl methacrylate) plasticised with n-butanol of a band characteristic of hydrogen bonding. The concentration of hydroxyl groups of the n-butanol taking part in the blocking of the polar groups of the polymer could be found by measuring the intensity of the absorption band; the concentration of alcoholic hydroxyl groups combined with the polar groups of the polymer is less than the total concentration of alcohol added to the polymer. The reduction in the glass temperature remains proportional to the concentration of added plasticiser only with a low content of n-butanol; further increase in the alcohol content produces a relatively smaller reduction in the glass temperature, but it remains proportional to the alcohol concentration determined spectroscopically, which corresponds to the amount of alcohol reacted with the polar groups of the polymer. It is these alcohol molecules which take part in the plasticising; the other alcohol molecules, although present in the system, do not. This work enabled Zhurkov to confirm his earlier suggestion that plasticising consists in the screening of the functional groups of the polymer by polar plasticiser radicals and to confirm his rule of "mole fractions".

Kargin remarks[48] that the introduction of plasticisers into a polar polymer produces the same effect as if the number of stronger polymer–polymer bonds were reduced.

Sedlis[49] considers plasticised systems as solid solutions, and the plasticising of polymers as analogous to mechanical orientation and chemical modification by copolymerisation.

Some workers (*e.g.* Simril[50]) relate the main role in plasticising only to the structure of the polymers themselves, and ascribe no influence to the structure of properties of plasticising additives or to the mechanism of their interaction with the polymers.

Merz[51] divides plasticisers into three types: primary, having good compatibility with the polymers and exhibiting a good plasticising action; secondary, not showing good compatibility but imparting definite properties to the polymers; and diluents, which reduce the cost of compositions

Sokolov and Fel'dman[52] considered the effect produced by plasticisers to be comparable with the reduction of freezing point observed in dilute solutions, and called the effect colligative, *i.e.* depending in the main on the number of added plasticiser molecules, but independent of the composition, structure, and molecular weight of the plasticising materials.

Aiken and coworkers showed[53] that plasticising does not always produce the same effect, which for a given polymer depends to some extent on the structure of the plasticiser.

Fuoss and Mead[54] thought that plasticisers of about the same molecular size and shape exhibit similar plasticising actions on a given polymer. However, polar polymers can only react with a plasticiser if its molecule contains polar or readily polarised groups, the plasticising effect consisting of the separation of the polymer macromolecules by plasticiser molecules, which produces a sharp decrease in the macroscopic and micro-coefficient of friction.

Gal'perin and Moseev[55] found that in the plasticising of cellulose nitrate an energetically saturated solvate layer requires one mole of dibutyl phthalate or two moles of acetone for each two gramme-molar $-ONO_2$ groups, *i.e.* both ester groups of the dibutyl phthalate participate in the blocking of the polar groups of the cellulose nitrate, only the $-ONO_2$ groups reacting with the plasticiser.

Kargin and Malinskii showed[56,57] that equimolecular fractions of different plasticisers reduce the glass temperature T_g of polymers to different extents, the reduction of T_g for non-polar and weakly polar polymers obeying, to a satisfactory approximation, the rule of "volume fractions", *i.e.* it is proportional to the fraction by volume of plasticiser added. As far as its viscosity is concerned, the addition of plasticisers to a polymer is equivalent to the appearance of holes in it, since the viscosity of a plasticiser can be ignored in comparison with the viscosity of a polymer. These workers consider that the rule of "mole fractions" correctly represents the mechanism of plasticising only of polymers whose micro-viscosity changes on plasticising mainly because of decreased intermolecular interaction, *i.e.* polymers whose units possess considerable polarity. When the intermolecular interaction between the polymer units is small (with non-polar or weakly polar polymers) the reduction in micro-viscosity on plasticising would be expected to arise mainly because of a steric effect, and hence for non-polar polymers T_g will depend linearly on the concentration by volume of the added plasticisers. The rules of "molar concentrations" and "volume concentrations" are reflections of two different mechanisms of plasticising, and each is obeyed by only a few systems, in which the action of one or other of these mechanisms predominates; many real systems will show greater or lesser deviations from both of the rules, because both mechanisms of plasticising apply simultaneously with comparable strength.

Boyer and Spencer[58] consider that the extent to which plasticisers act on polymers depends on the plasticiser concentration, the plasticisers causing separation of the polymer chains and hence a reduced energy barrier in the polymer system.

According to Slonimskii's results[59,60] plasticisers affect a polymer in two ways: they cause a reduction in the intermolecular viscosity, and by reacting with individual chemical groups of the macromolecular chains they can produce either a decrease or an increase in the intramolecular viscosity.

Kargin and Slonimskii[61] have confirmed the applicability of the rules of "mole fractions" and "volume fractions" to various plasticised polymer systems; these rules represent extreme limiting cases of plasticising, and in real polymers they overlap.

(b) The Plasticising of Crystalline Polymers, Graft and Block Copolymers

It has been suggested[62] that the crystal structure of a polymer changes in the presence of plasticisers which cause it to swell. With plasticiser oils in the system an amorphous halo appears on the fibre diagram of the polymer. However, in the study of vinyl polymer–tricresyl phosphate systems[63] no changes in the initial structure of the polymer under the action of plasticisers could be detected on the X-ray diagrams.

The sorption of the vapour of low-molecular-weight plasticisers depends on the structure of the polymers; orientated crystalline polymers are more active in sorption than other types of polymer[64]. The addition of plasticisers (dimethyl phthalate, dibutyl sebacate, cetyl chloride) to crystalline polymers reduces their glass temperature in the same way as is observed with amorphous polymers[65], but with crystalline polymers the melting point is only very slightly reduced, *i.e.* the plasticising of crystalline polymers does not decrease but increases the difference between T_g and the melting point. The displacement of T_g with crystalline non-polar polymers obeys the same rule of "volume fractions" as with amorphous non-polar polymers and is independent of the nature of the plasticiser; however, with large plasticiser concentrations there is some deviation from this rule.

Study of the plasticising of systems in which the macromolecules contain both polar and non-polar sections[66] has shown that polar plasticisers (glycerol) and non-polar plasticisers (tetralin) act independently, the plasticising of the non-polar parts of the copolymer obeying the rule of "volume fractions", and the polar parts the rule of "mole fractions". Tetralin plasticises only the polystyrene units in accordance with the rule of "volume fractions", while glycerol under the same conditions acts primarily on the polar groups of polyvinyl alcohol and polyacrylic acid. When both plasticisers are present each supplements and strengthens the action of the other.

The plasticising of block copolymers in which the units are of greatly differing polarity using polar and non-polar plasticisers has been studied[67], using acrylic acid–styrene block copolymers, with glycerol and tetralin as plasticisers. With glycerol there is a sharp decrease in the glass temperature of the block copolymer, the first portions of glycerol reducing the glass temperature in proportion to the mole fraction of glycerol, but with a further considerable increase

in the glycerol content the reduction of T_g gradually tails off. An analogous effect was observed with the mixed type plasticiser dibutyl phthalate. When glycerol acts on the block copolymers it dissolves mainly in micro--regions enriched in acrylic acid, reducing T_g for the polyacrylic acid micro-regions and considerably lowering the softening point of the specimen as a whole, although regions enriched in polystyrene are practically unaffected. With the non-polar plasticiser (tetralin) which dissolves in the polystyrene micro-regions, there is no reduction in the softening point of the sample as a whole, since the hard polyacrylic acid micro-regions remain practically unaffected. Only when the polar and non-polar plasticisers act together are both types of micro-region plasticised, giving a general reduction [? of the softening point (Ed. of Translation)] of the block copolymer as a whole.

Although there have been few studies of the plasticising of crystalline polymers, graft and block copolymers, the data given above show that it involves the same processes and characteristics as the plasticising of amorphous polymers. The rules of mole fractions and volume fractions apply to this type of high-molecular-weight substance also, to a certain extent.

(c) The Influence of the Chemical Structure of Plasticisers on the Plasticising of Polymers

Of great significance for the further development of the study of plasticising is the investigation of the part played by the chemical structure of the plasticisers and particularly the relationship between the plasticising effect and the structure of the plasticisers (the plasticising effect can be measured by the change in T_g or in mechanical or other properties of the polymers under the action of a definite quantity of plasticiser).

Thus it has been remarked[44,66-70] that the chemical structure of polymers and plasticisers actively affects only the compatibility of the components, and not the magnitude of the plasticising effect. There has been no observed influence of the chemical structure of the plasticisers on the plasticising of polymers when mixtures of plasticisers are used[71]. However, on systematic study of the process such an influence can be found in the most varied classes of organic substances[72].

The influence of the chemical nature and molecular size and shape of plasticisers on the plasticising of polymers has been studied[73-75] using trioctyl phosphate, tricresyl phosphate, and certain other plasticisers; different effects were observed, in particular polymeric materials containing different plasticisers had substantially different freeze--resistance properties.

Plasticisers of low- and of higher-molecular-weight behave differently in polymer compositions[76]. The part played by the chemical structure of plasticisers has been noted in various studies[77-78].

The plasticising of divinylbenzene-styrene rubber varies with different types of plasticisers (non-polar plasticisers are the best)[72]. With small concentrations of plasticiser in SKS-30A rubber the rule of volume fractions is obeyed fairly satisfactorily, the reduction in T_g not depending on the nature of the plasticiser[80]. With higher plasticiser concentrations there are deviations from this rule, and T_g for the rubber is lower with non-polar plasticisers than with polar. With not more than 20 vol. % of plasticiser in the vulcanisate the reduction in the tensile strength and the change in the relative extension are independent of the plasticiser structure; however, with a plasticiser content above 20 vol. %, and particularly above 50 vol. %, the plasticising effect does depend on the molecular structure of the plasticiser.

The effect of the chemical structure of the plasticisers on the plasticising of polymers has also been noted in a number of other studies[82-83] in which simple views of the mechanism of plasticising are also given.

The mechanical properties of certain polymers have been studied[84] as a function of the chemical structure of the plasticisers, in particular the influence of carbon chain length and number of polar groups using methyl, butyl, and ethylhexyl methacrylates as plasticisers. Changes in the structure of the plasticiser produce corresponding changes in the 100% modulus and tensile strength of the polymers, and the force *vs.* deformation curve varies in shape with compositions having different amounts of the different plasticisers.

Frissell[85] found a relationship between the minimum flow temperature of polymers and the structure of plasticisers having the same molecular weight, and showed that increased chain length of the esterifying groups in the plasticisers (esters of phthalic acid) increases the minimum flow temperature of the polymers.

The complex nature of the bonding in polymer–plasticiser systems has been pointed out[86,87]. Small amounts of different plasticisers are held strongly by the polymer, although to different extents, but with increasing plasticiser content a point is reached when additional plasticiser does not become bonded with the polymer chains; it is this part of the plasticiser which first migrates when the polymer is in storage or use. In the study of dielectric losses in plastics it was found that the plasticiser molecules associate with a definite number of polymer groups (depending on the chemical nature of the plasticiser)[88].

Würstlin and Klein[89] observed that T_g for amorphous polymers depends on the chemical structure of the plasticisers.

Thinius states[90] that the mechanism of plasticising is closely bound up with the structure of the polymers, and can be described by two theories: (1) the thermodynamic, which allows for physical and chemical interactions in the polymer–plasticiser system, and (2) the theory of action of plasticisers as lubricants, which does not. There are also theories which combine these two extremes, in which the role of the plasticisers is mainly to reduce the steric hindrance to rotation of the functional groups of the macromolecular chains. The dependence of the plasticising effect on the chemical nature of the plasticiser is particularly evidenced by the fact that different plasticisers affect the individual properties of polymers to different extents[90]. In their electron microscopic investigation of cellulose nitrate–dibutyl phthalate and cellulose nitrate–softener† systems, Ames and Sampson found[91] that the texture of the resulting films varied with the solvent power of the plasticisers, *i.e.* in the last analysis, with their structure.

In generalising data on plasticising, Voyutskii remarks[92] that the compatibility of polymers with plasticisers depends on the energy interaction between molecules of the two components and on the entropy of mixing. The plasticising

† Castor oil (Ed. of Translation).

effect also depends on the shape and size of the molecules of polar plasticisers, the polar group causing reaction with the polar group of the polymer (*i.e.* compatibility), and the non-polar part producing the actual plasticising effect by screening the interacting dipoles of the polymer macromolecules.

The influence of the chemical structure of plasticisers on the plasticising effect has also been quantitatively investigated in a number of other studies[93-98], which have demonstrated the dependence of the plasticising effect on the structure, polarity, size, and shape of the plasticiser molecules. The dependence of the plasticising effect on the position of functional groups in plasticiser molecules has been demonstrated[97], and in particular that α-naphthol is a more effective plasticiser for poly(vinyl chloride) than β-naphthol (although β-naphthol is more polar than α-naphthol); this is explained by the particular electronic structure of these molecules. A substantial influence on the plasticising effect is exerted by the structure of side chains (branching) in the molecules of certain plasticisers[100]; thus epoxidised tetrahydrophthalates with branched side chains are less effective than the corresponding plasticisers with linear chains.

Tager and coworkers used a thermomechanical method to study the influence of diphenic and naphthalic diesters and diphenic monoesters on T_g for polystyrene and polymethyl methacrylate containing 25 mole % of plasticiser[101,102], and showed a connection between the activity of a plasticiser and its compatibility with the polymers: the lower the critical mixing temperature, the lower is T_g. As the size of the alkyl radical of the ester increases, T_g decreases regularly to a certain alkyl chain length and then increases. The explanation of this is that the plasticiser molecules enter between and separate the macromolecules of the polymer, so decreasing the viscosity of the system. The vibratory motion of the units of the polymer chain is thereby facilitated and is retained down to lower temperatures, causing a reduction in T_g: the larger the alkyl radical, the greater is the separation of the macromolecules and the lower is T_g. However, very large alkyl radicals will increase T_g because of the unfavourable geometrical disposition of the longer plasticiser molecules in the polymer phase; to a considerable extent this depends on the particular structure of the plasticiser molecules. The high plasticising action of diphenic acid diesters is due to the great mobility of their molecules and their low rigidity, so that the molecules of the diphenic acid diesters can assume many different conformations and can be arranged in a large number of ways amongst the polymer molecules; this creates favourable conditions for improved compatibility of the components and a stronger plasticising action by the plasticiser on the polymer. With naphthalic acid esters, which contain the rigid planar dinuclear condensed ring system, the number of possible conformations is considerably less; hence they are less compatible with the polymers and their plasticising effect is less. In these studies[93,97-102] it is noted that the rule of mole fractions is not observed accurately in the systems investigated, since the plasticising effect depends substantially on the chemical structure and the size and shape of the molecules of plasticiser.

3. PLASTICISING IN THE LIGHT OF NEW VIEWS ON THE STRUCTURE OF LINEAR POLYMERS

The discovery of the globular packet structure of linear polymers[17] enables a number of facts on the nature and mechanism of the physical plasticising of polymers to be interpreted anew at a deeper level. Although there have been few studies in this field, the first positive results have already been obtained.

The plasticising of the rigid-chain polymer cellulose, which is poorly compatible with plasticisers, has been studied[103], using as plasticisers urea and guanidinium thiocyanate in quantities of 8 to 60%, in solution in ethanol. The thermomechanical properties of the system indicate that the plasticising effect does not correspond with the rules of mole fractions or volume fractions, and it was found in another work[104] that the plasticising of cellulose with triethylphenylammonium oxide can increase the elastic properties of the polymer. This demonstrates the existence of two greatly different mechanisms of the plasticising of cellulose. In the one case the introduction of the plasticiser leads to a regular decrease in T_g for cellulose, and the mechanism of plasticising can be explained by the rules of mole fractions and volume fractions. In the other case (with urea as plasticiser) the plasticising effect cannot be explained as the result of interaction between plasticiser molecules and polymer macromolecules (the plasticisers do not mix unrestrictedly with the polymer). The plasticising effect of this type of plasticiser is explained in terms of the packet theory of the structure of linear polymers, and two possible mechanisms of plasticising are suggested. According to one of these, plasticising occurs within the packets when the interaction between plasticiser molecules and the active groups of the polymer chains is greater than the intermolecular action in the polymer itself. The plasticising effect of such plasticisers which are fully miscible with the polymer is to destroy any secondary structural formations (including packets) in the polymer and form a solid solution of polymer and plasticiser. If the reaction of the plasticiser molecules with the active groups of the polymer chains is substantially weaker than the intermolecular interaction in the polymer itself, then the plasticiser is able to react only with molecules on the surface of the secondary structures (the packets of chains), and only plasticising between the packets occurs, without any significant change in the elastic properties of the system.

In plasticising between the packets a more important part is played by the packets themselves, these possessing elasticity of shape and being stable to temperature changes[105]. The polymeric materials obtained by plasticising between the packets should have high shock and freeze resistance. In the plasticising of cellulose triacetate with phenylethylphenols, which dissolve the polymer and lower its transformation points, the brittleness of the films is reduced less than in plasticising with dihexyl sebacate, which is only partially compatible with the polymer[106-108]; hence in the former case packet formation of macromolecules is limited, because the reaction of the plasticiser with the macromolecules of the polymer exceeds the intermolecular interaction of the polymer chains. The plasticiser is then distributed between the polymer chains, and by facilitating relaxation processes it provides for a relatively dense packing of the chains, so that the films show little shrinkage. In plasticising cellulose triacetate with the partially compatible dihexyl sebacate, whose reaction with the active groups of the polymer chains is less than the intermolecular interaction, there is no hindrance to the formation of packets. With a predominantly packet structure in the films relaxation processes become difficult, so that the plasticised material has a large shrinkage. Because of the looseness of the packing the elasticity of the

packets is substantially increased, which causes a reduction in the brittleness of the films and improved mechanical properties.

In general, when substances of limited compatibility are combined with cellulose triacetate, plasticising occurs between the packets[108], since the plasticisers cannot penetrate into the packets; with fully compatible plasticisers plasticising occurs within the packets, and the properties of the resulting polymer systems are different.

Study of the plasticising of polycarbonates, which are characterised by reduced relaxation and crystallisation processes and which tend to form definite secondary structures, has shown that plasticising can occur within and between the packets[109]; the action of different plasticisers usually involves a combination of these two extreme types of plasticising, with a greater or lesser approximation to one or the other. Thermomechanical investigations have established that the introduction of a plasticiser which gives mainly plasticising between the packets somewhat reduces the elasticity modulus of the polycarbonate films, which then remains constant over a wide range of plasticiser concentrations. The introduction of a plasticiser which more nearly corresponds to plasticising within the packets reduces the elasticity modulus of the films regularly, the reduction being strictly proprotional to the amount of plasticiser introduced.

The study of structure formation (the nature of the secondary structures) in plasticised crystalline polystyrene has shown[110] that the plasticising affects the characteristic conditions for the formation of secondary structures in the unplasticised polymer; dimethyl phthalate, dibutyl sebacate, and cetyl chloride were used as plasticisers, in amounts of 8–20% by volume. Plasticising of crystalline polystyrene, particularly at low temperatures and with a low plasticiser content, produces a sharp change in the structure of the secondary formations, considerably increasing the rate of growth of spherolites and preventing their aggregation into ribbons or plates (*i.e.* in the presence of plasticisers the crystallisation ceases with the formation of large spherically symmetrical particles). With plasticiser concentrations of less than 10% the strength of crystalline polystyrene is much reduced, because of changes occurring in the supermolecular structures of the polymer, with the formation mainly of spherolites separated by plasticiser molecules. The destruction of such spherolitic plasticised systems apparently proceeds along the boundaries of the spherolites.

The theory of plasticising between and within the packets has also been applied[111] to linear thermoplastic polar polymers of the poly(vinyl chloride) type. Small additions[5-10] of polar plasticisers have the effect of plasticising the polar polymer between the packets, or in general between the structures, while larger additions of the same plasticisers lead to plasticising within the packets (or structures). With this type of plasticising the strength of the polymer first increases to a definite limit, and then decreases as plasticising within the packets becomes more prominent.

Lipatov[112] has used the dilatometric method to investigate polystyrene or poly(methyl methacrylate) films filled with glass powder (50% of the total weight of the mixture) and containing various amounts of dimethyl phthalate as plasticiser. The filled polymers have higher values of T_g than the unfilled polymers, due to the reduced mobility of the chains and packets because of interaction with the surface of the filler. With both polymers, with more than a certain content of plasticiser T_g for the filled polymers becomes less than T_g for the unfilled polymers. It is suggested that the higher T_g for the filled polymers is due to the limited mobility of the packets near the surface of the filler caused by adsorption interaction and steric hindrance. During the formation of the polymer films in the presence of the filler, the packets or other secondary structures produced in the concentrated solutions become attached to the surface of the filler[113]. The presence of a plasticiser cannot prevent these effects of secondary structure formation in the solutions, and hence the plasticiser is not distributed evenly between all the macromolecules of the polymer. In the case of a filled polymer the interaction of the added plasticiser with the filler surface will to some extent prevent interaction of the packets with the surface, so that the packets of chains interacting with the surface in the presence of plasticiser will have a high mobility in comparison with that of the packets in the absence of plasticiser, or with that of the packets in the presence of the same amount of plasticiser but in the absence of filler. It can be assumed that with the filled polymer, where there is a sufficiently well-developed contact surface between the polymer molecules and the filler, the effects of breaking the bonding between the packets and the surface, like the effects of plasticising between the packets, will play the dominant role. Since it is this bonding which causes the sharp increase in T_g in the filled polymer, the breaking of this bonding should produce just such a sharp decrease in T_g for the plasticised filled polymer; therefore the effects of plasticising between the packets are more marked with filled polymers, which are characterised by looser packing on the filler surface. In this case, as the content of plasticiser in the polymer increases, the part played by plasticising on the boundary between the polymer and the filler surface is gradually reduced, and the more important part is played by the effects of the plasticising of the polymer itself, *i.e.* the breaking of intermolecular bonds in the polymer itself. Since the interaction of the polymer with the filler surface also takes place with a relatively large plasticiser content, further weakening of the bonding with the surface is superimposed on the actual plasticising of the polymer, and with an equimolecular content of plasticiser the over-all reduction of T_g becomes greater in the presence of the filler than in the case of the unfilled polymer. It is concluded from the above that the plasticising of filled polymers is determined by two effects: plasticising between the packets, caused by the breaking of filler surface–polymer bonding, and normal plasticising, caused by the breaking of polymer–polymer bonds.

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The study of the plasticising of polymers by low-molecular-weight substances has made considerable strides forward, so that the rules of mole fractions and volume fractions have been formulated, plasticising between and within packets has been discovered, and the effect of the chemical structure of plasticisers on the plasticising of polymers has been more clearly demonstrated.

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MONOALKYLHYDRAZINES

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I. INTRODUCTION

Alkylhydrazines, being close analogues of aliphatic amines, have been known for a comparatively long time, but their study really began only recently, when these reactive substances were found to exhibit interesting features in their chemical and biochemical behaviour.

Alkylhydrazines, and especially aralkylhydrazines, are able to inhibit the enzyme monoamine oxidase. This has led to the discovery of effective nerve stimulants, which are widely used in modern psychiatry. Introduction of such compounds as phenylisopropylhydrazine into the animal or human organism increases the concentration of serotonin in nerve tissue[1-3]. An intensive search is therefore being undertaken in various laboratories in the world for new medicinal preparations containing an aralkylhydrazino--group, with the aim of synthesising analogues or antagonists of serotonin [4,5], as well as of likely antimetabolites of purine bases[6].

Recently, effective uterine stimulants have been discovered among the alkoxyaralkylhydrazines, resembling oxytocin in their action[7-9]. Alkylhydrazine derivatives have also found practical application in the synthesis of other drugs. Special mention must be made of systemic insecticides. Those based on alkylhydrazines are similar to the organophosphorus poisons in their effect, but are less toxic to warm-blooded animals.

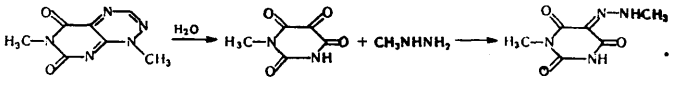
In spite of the large amount of work which has been done on the monoalkylhydrazines, the literature in this important field has not yet been surveyed. Existing review papers and monographs on the chemistry of hydrazine compounds [10-14] deal mainly with the chemistry of hydrazine hydrate and to some extent with phenylhydrazine, but contain only fragmentary information on alkylhydrazines.

In the present review the general term "monoalkylhydrazines" is used to cover monosubstituted hydrazine derivatives containing purely aliphatic and substituted aliphatic radicals, aralkyl and substituted aralkyl radicals, and also alicyclic and hydrogenated heterocyclic radicals. Arylhydrazines, *i.e.* compounds of the type of phenylhydrazine, which have been widely studied and have specific methods of preparation and properties, will not be dealt with here. Hydrazinium salts have been reviewed elsewhere[15].

II. METHODS OF PREPARATION

Alkylhydrazines are not found in Nature, but methylhydrazine has been isolated from the hydrolysis products of the antibiotic toxoflavine, which is produced by the

bacterium *Pseudomonas cocovenenans* [16,17]. The toxoflavine molecule is rapidly cleaved by mineral acids, with the formation first of *N*-methylalloxan and methylhydrazine, and then of "toxoflavine B", which is a methylhydrazone of *N*-methylalloxan:

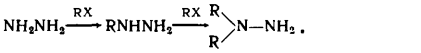


Methods of synthesising monoalkylhydrazines can be divided into two broad groups. The first comprises those in which hydrazine itself is the starting material. The second group can include methods in which the hydrazino--radical is synthesised from compounds containing no N–N bond.

1. Direct and Indirect Replacement of Hydrogen Atoms in Hydrazine

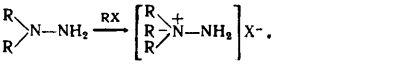
Alkylation of hydrazine. After the discovery by E. Fischer of the readily accessible phenylhydrazine, research workers concentrated their interest mainly on aromatic representatives of this class of compounds. In contrast, only complicated, inadequate methods of preparation were known for most of the alkylhydrazines.

Westphal [18,19] investigated the reaction of hydrazine with alkyl halides, but was mainly concerned, not with the monoalkylhydrazines, but with products of their further alkylation. In fact, alkylation of hydrazine first yields a monoalkylhydrazine, which readily undergoes further alkylation to form an unsymmetrical dialkylhydrazine [20,21]. Symmetrical dialkylhydrazines are not usually formed under these conditions.

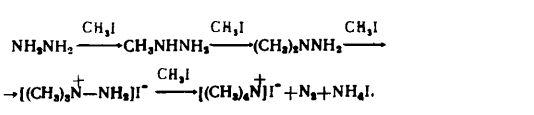


In the case of phenylhydrazine, on the other hand, symmetrical alkylation (*i.e.* formation of 1-alkyl-2-phenylhydrazines) also occurs, since the phenyl group makes alkylation of one of the nitrogen atoms more difficult.

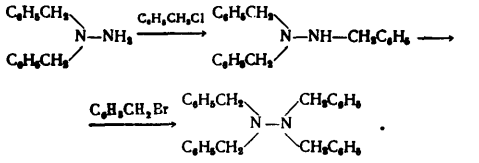
Unsymmetrical dialkylhydrazines, on further alkylation, add on the new alkyl radical to the already substituted nitrogen atom, yielding a quaternary hydrazinium salt:



Active alkylating agents (for example, alkyl iodides) give such quaternary salts directly and almost exclusively on reaction with hydrazine [22]. After formation of the hydrazinium salt, reaction ceases, the second amino-group remaining unsubstituted. This was first established by Harries and Haga [20] for the methylation of hydrazine with methyl iodide in the presence of an excess of caustic potash. Methylhydrazine, dimethylhydrazine, and, as final product of the reaction, trimethylhydrazinium iodide were isolated. An attempt at further methylation of this quaternary salt at 130° gave only tetramethylammonium iodide, so that the hydrazine molecule had been cleaved with rupture of the nitrogen–nitrogen bond:

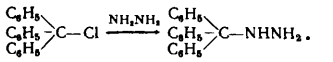


In isolated cases a trialkylhydrazine can be obtained by direct alkylation. Thus Franzen and Kraft [23,24] subjected hydrazine hydrate to prolonged treatment with benzyl chloride, and obtained tribenzylhydrazine, from which Wieland and Schamberg [25] subsequently prepared tetrabenzylhydrazine by the action of benzyl bromide:



This result is due primarily to steric hindrance, which prevents the attachment of a third benzyl radical to an already substituted nitrogen atom and hence the formation of a quaternary salt.

The effect of steric hindrance in raising the yield of monoalkylhydrazine is especially evident in the reaction of hydrazine with chlorotriphenylmethane [26,27]. In this case the yield of methyltriphenylhydrazine is 87%, and there is practically no further alkylation:



By exploiting similar favourable steric factors, Klages [28,29] synthesised triisopropylhydrazine, and from 1,2-dimethylhydrazine and isopropyl bromide obtained 1,2-diisopropyl--1,2-dimethylhydrazine. Elimination of halogen with formation of the hydrocarbon takes place as a side-reaction in the interaction of hydrazine with tertiary halides [27].

Thus direct alkylation of hydrazine usually yields monoalkylated and unsymmetrically dialkylated hydrazines, and as the last stage hydrazinium salts, which do not react with alkylating agents (or else break down with rupture of the N–N bond). In practice, alkylation of hydrazine with an equivalent quantity of an alkyl halide gives a mixture of these compounds, only a small proportion of the monoalkylhydrazines being obtained [18,23,24,28–30]. When hydrazine is treated with the higher 1-chloroalkanes (above C_8), practically no quaternary salt is formed, and with alkyl chlorides containing more than twelve carbon atoms the main reaction products are monoalkylated and unsymmetrically dialkylated hydrazines [18,19].

The above facts make clear why the view has become established in the literature that direct alkylation of hydrazine cannot serve for the preparation of monoalkylhydrazines [13,15,30,31]. Nevertheless, other results have been published for this reaction. Thus Gabriel [32] worked out a method for obtaining allylhydrazine from hydrazine hydrate and allyl chloride, the yield being 34%. Votoček and Lemiger [33] reported the synthesis of phenethylhydrazine in 41% yield from hydrazine hydrate and phenethyl chloride. Westphal [18] obtained hexyl-, octyl-, dodecyl-, and hexadecyl-hydrazine from hydrazine hydrate and the corresponding chlorides, the respective yields being 26, 26, 47, and 62%. The synthesis of butyl- and octyl-hydrazine as their sulphates, from hydrazine sulphate and the corresponding halides, has been reported in the patent literature [34]. It has been stated [1] that the aralkylation of hydrazine with secondary halides gives yields of 35–45%, but the reaction is complicated by elimination of hydrogen halide with formation of a carbon–carbon double bond.

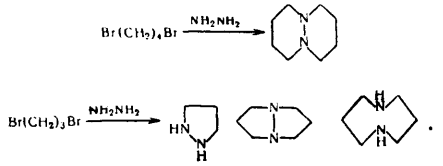
Polyalkylation is considerably diminished[35] by slow addition of the alkyl halide to a tenfold excess of hydrazine hydrate with vigorous stirring of the reaction mixture. However, complete removal of the resulting monoalkylhydrazine from the reaction mixture is sometimes achieved only by continuous and prolonged extraction in a suitable apparatus. It is probable that here the usual partition of alkylhydrazine between solvent and hydrazine hydrate is accompanied by equilibrium between a salt of the alkylhydrazine and the hydrazine itself, which prevents rapid extraction of the alkylhydrazine. In some cases a considerably smaller excess of hydrazine can be used. Thus isopropylhydrazine has been obtained in 68% yield by the reaction of isopropyl bromide with a fourfold excess of hydrazine hydrate. This can probably be explained by steric hindrance, which prevents the formation of diisopropylhydrazine. It is true that here, owing to the lower reactivity of the halide, the reaction mixture must be heated. In several cases (with butyl- and nonyl-hydrazine) the use of alcohol as solvent cannot be avoided, since otherwise only a dialkylhydrazine is obtained[36]. Kost and Sagitullin proposed this method for the synthesis of alkylhydrazines[36-38] and aralkylhydrazines[8,39,40].

Biel and his coworkers[1,41] have recently made similar observations on the possibility of the direct synthesis of alkylhydrazines (see also Refs. 42 and 43).

Dreyfus[44,45] patented the preparation of dihydrazines from hydrazine hydrate and dihalides in which the halogen atoms were attached to two different methylene groups:

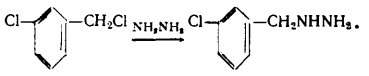
$$Cl(CH_2)_6Cl \xrightarrow{NH_2NH_2} NH_2NH(CH_2)_6NHNH_2.$$

It was shown later that reaction of hydrazine with such dihalides may also yield heterocyclic compounds. Thus 1,4-dibromobutane and hydrazine hydrate gave decahydro-9,10-diazanaphthalene[46], while from 1,3-dibromopropane were obtained pyrazolidine, trimethylenepyrazolidine, and 1,5-diazacyclooctane[47]:



Formation of this last compound can be explained by the reducing action of diimide HN : NH.

If a halogen atom is attached to an aromatic nucleus, it usually remains unaffected. Thus reaction of hydrazine with *m*-chlorobenzyl chloride produces *m*-chlorobenzylhydrazine[48]:



Monoalkylhydrazines can be synthesised without complication from hydrazine and halogen derivatives containing a hydroxy-group or a substituted amino-group, for example a diethylamino-group[41,49,50]:

$$(C_2H_5)_2NCH_2CH_2Br \xrightarrow{NH_2NH_2} (C_2H_5)_2NCH_2CH_2NHNH_2.$$

However, reaction of 4-chlorobutanol with hydrazine in the presence of alkali at 95–100° gave only tetrahydrofuran, whereas in the absence of alkali at 30° 4-hydrazinobutanol is formed[51].

α-Halogenated acids react with hydrazine to form α-hydrazino-acids, which are hydrazine analogues of α-amino-acids[52-54]. The use of ion-exchange resins for their isolation has been developed[55]:

$$R{-}\underset{\displaystyle Br}{\underset{|}{CH}}{-}COOH \xrightarrow{NH_2NH_2} R{-}\underset{\displaystyle NHNH_2}{\underset{|}{CH}}{-}COOH.$$

Chloroacetic acid and hydrazine give mainly hydrazinediacetic acid[56-58], which serves as an intermediate in the synthesis of azocarboxylic ester:

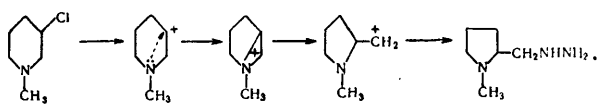
$$ClCH_2COOH \xrightarrow{NH_2NH_2} \underset{\displaystyle HN{-}CH_2COOH}{\underset{|}{HN}}{-}CH_2COOH.$$

The reaction of hydrazine with halogenated derivatives of this type is complicated by secondary processes. Thus treatment of α-bromoacetoacetic[59] and benzoylbromoacetic[60] ester, bromo-diketones[61,62], β-halogeno-α-nitro-derivatives of aliphatic acids[62], and chloronitromethane[63] with hydrazine hydrate results in replacement of the halogen by hydrogen.

α-Halogeno-ketones form with hydrazine a mixture of various compounds, including pyrazines[64].

Sometimes the reaction of hydrazine with halogenated derivatives is accompanied by rearrangement. Thus treatment of 3-chloro-1-methylpiperidine with hydrazine results in contraction of the piperidine ring, with formation of 2-hydrazinomethyl-1-methylpyrrolidine[41]. The structure of this compound has been proved by reduction to the corresponding amine, which has been prepared in a different way, and also by synthesis of a compound known to be 3-hydrazino-1-methylpiperidine.

It is probable that an initially formed carbonium cation is stabilised by the lone pair of electrons from the nitrogen atom, after which cleavage of the three-membered ring leads to a Dem'yanov rearrangement:



In several cases esters of mineral acids are used instead of alkyl halides for the alkylation of hydrazine. A 32% yield of ethylhydrazine has been reported from the action of diethyl sulphate on an alkaline alcoholic solution of hydrazine[65], and propylhydrazine has been obtained by the interaction of hydrazine hydrate and potassium propyl sulphate[66,67]. The reaction of hydrazine with nitric esters[68,69] is considerably more complicated. Primary aliphatic (ethyl, butyl, isopentyl) nitrates, with a sufficiently high concentration of hydrazine, undergo mainly reduction with the formation of gaseous nitrogen, nitrous oxide, ammonia, the nitrite and nitrate ions, and also alkylated hydrazines, alcohol, and traces of aldehyde. In the case of benzyl nitrate, it has proved possible to isolate benzylhydrazine (as the nitrate) and di-, tri-, and tetra-benzylhydrazines, together with benzaldehyde dibenzylhydrazone. This reaction is unsuitable for the preparation of monoalkylhydrazines.

Finally, hydrazine can add on to an activated double bond. Thus it adds on to β-nitrostyrene and to styrene itself to form the corresponding phenethylhydrazines[70,71]:

$$C_6H_5{-}CH{=}CH_2 \xrightarrow{NH_2NH_2} C_6H_5CH_2CH_2NHNH_2.$$

Nitriles of unsaturated aliphatic acids (acrylic, crotonic, cinnamic), as well as their esters and amides, are able to add on a molecule of hydrazine to form monosubstituted hydrazines[72-78]. For example, the reaction of hydrazine with acrylonitrile (cyanoethylation) gives β-hydrazinopropionitrile in yields up to 90%:[74]

$$CH_2{=}CHCN \xrightarrow{NH_2NH_2} NH_2NH{-}CH_2CH_2CN.$$

With excess of acrylonitrile a second molecule of the latter adds on both at the NH and at the NH_2 group[79]. In the presence of sodium ethoxide, cyanoethylation is accompanied by cyclisation giving 3-aminopyrazoline as a secondary product[78].

Dimethyl fumarate, however, does not add on hydrazine on heating, but is converted into the dihydrazide of fumaric acid[80]. A non-conjugated double bond in unsaturated acids is reduced in good yield on being heated with hydrazine hydrate[81-85]. The action of hydrazine on fluoroalkenes has been studied[85].

Hydrazine adds on smoothly to ethylene oxide and its homologues, the oxide ring undergoing cleavage with the formation of 2-hydrazinoethanols[32,51,86-92]:

$$\underset{\diagdown O \diagup}{CH_2{-}CH_2} \xrightarrow{NH_2NH_2} HOCH_2CH_2NHNH_2.$$

Thus hydrazinoethanols have been used for the synthesis of several hydrazides[93] and semicarbazones[51] in the search for antibacterial agents. With acetylenic oxides hydrazine forms *N*-aminopyrroles[90]. The interaction of hydrazine with epoxypropionic esters has been described[94].

Alkylation of hydrazine derivatives. Because of the above difficulties in the direct alkylation of hydrazine, workers long ago searched for various indirect methods, including processes involving temporary protection of the amino-group.

A typical example of such alkylation is the method proposed by Thiele in 1910[30] for preparing methylhydrazine†. It is based on the conversion of benzylidene azine into a hydrazinium salt by reaction with dimethyl sulphate, the quaternary salt being decomposed by water into one mole of methylhydrazine and two moles of the aldehyde. The methylhydrazine is isolated as the sulphate, the yield of which is 51–54%:[12,30,95,96]

$$C_6H_5CH{=}NN{=}CHC_6H_5 \xrightarrow{(CH_3O)_2SO_2} [C_6H_5CH{=}\overset{+}{N}(CH_3){=}CHC_6H_5]CH_3SO_4^- \xrightarrow{H_2O}$$

$$\longrightarrow CH_3NHNH_2 + 2C_6H_5CHO + CH_3OSO_3H.$$

This convenient method is of extremely limited application, since reaction does not take place with diethyl sulphate, and this applies especially to the higher dialkyl sulphates. Ethylhydrazine can be obtained in low yield by alkylating benzylidene azine with ethyl iodide. This is mentioned by Thiele[30] without any indication of the experimental details. Azines of aliphatic aldehydes[97] and ketones[98], on treatment with alkyl halides, undergo intramolecular cyclisation with the formation of 1-alkylpyrazolines.

† In the opinion of Weygand[95], only one preparative method exists in the chemistry of the alkylhydrazines, and this is Thiele's preparation of methylhydrazine.

As azines are derivatives of carbonyl compounds, they are able, like aldehydes and ketones, to add on organomagnesium compounds. Addition of one molecule of phenylmagnesium bromide to ethylidene azine followed by treatment with water gives a 30% yield of a hydrazone, hydrolysis of which produces α-methylbenzylhydrazine[99]:

$$CH_3CH{=}N{-}N{=}CHCH_3 \xrightarrow[H_2O]{C_6H_5MgBr} C_6H_5{-}CH(CH_3){-}NH{-}N{=}CHCH_3 \xrightarrow{NaOH}$$

$$\longrightarrow C_6H_5CH(CH_3){-}NHNH_2.$$

Similarly, α-methylphenethylhydrazine was obtained from benzylmagnesium chloride[100,101], and from isopropylidene azine and with methylmagnesium bromide the product was t-butylhydrazine[102].

The reaction of benzylidene azine with organomagnesium compounds is more complicated, the products including hydrocarbons as well as aralkylhydrazones, which can be explained by partial breakdown at an azo-link, caused by migration of the double bond to the N : N position[103]:

$$C_6H_5CH{=}N{-}N{=}CHC_6H_5 \xrightarrow[H_2O]{RMgX} C_6H_5{-}\underset{\displaystyle R}{\underset{|}{CH}}{-}NH{-}N{=}CHC_6H_5 \longrightarrow$$

$$\longrightarrow \left[C_6H_5{-}\underset{\displaystyle R}{\underset{|}{CH}}{-}N{=}N{-}CH_2C_6H_5\right] \longrightarrow C_6H_5{-}\overset{\displaystyle H}{\overset{|}{\underset{\displaystyle R}{\underset{|}{C}}}}\cdot + N_2 + \cdot CH_2C_6H_5.$$

Grandberg and Kost[104] worked out a synthesis of benzylhydrazine by the benzylation of the sodium derivative of the enol form of acetone acetylhydrazone. Hydrolysis of the reaction product with hydrochloric acid gave a 76% yield of benzylhydrazine:

$$NH_2NH_2 \xrightarrow{CH_3COOC_2H_5} CH_3{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}NHNH_2 \xrightarrow{(CH_3)_2CO} CH_3{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}NHN{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH_3 \xrightarrow{NaOH}$$

$$\rightarrow CH_3{-}\underset{\displaystyle ONa}{\underset{|}{C}}{=}N{-}N{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH_3 \xrightarrow{C_6H_5CH_2Cl} CH_3{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}N(CH_2C_6H_5){-}N{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH_3 \xrightarrow[H_2O]{HCl} C_6H_5CH_2NHNH_2.$$

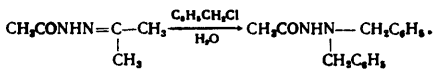
A year later Ronco and Erlenmeyer[105-107] used an analogous reaction to prepare 1-alkyl-1-acylhydrazones. They used biacetyl as carbonyl component, and carried out the hydrolysis under very mild conditions, which enabled the acyl group to be preserved. Better results were achieved by boiling the biacetyl 1-acyl-1-alkylhydrazone in aqueous alcohol with semicarbazide, which combined with the biacetyl that was eliminated:

$$RCONHNH_2 \xrightarrow{CH_3COCOCH_3} RCONHN{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}O \xrightarrow{R'Br}$$

$$\longrightarrow RCO{-}\underset{\displaystyle R'}{\underset{|}{N}}{-}N{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}O \xrightarrow{H_2O} RCO{-}\underset{\displaystyle R'}{\underset{|}{N}}{-}NH_2.$$

A detailed study of the reaction of benzylhydrazine with acylhydrazones has shown[108] that the latter, when in the form of the sodium derivatives of the enols in anhydrous medium, take up the benzyl radical at the nitrogen atom linked to the acyl group, whereas under severe conditions a second benzyl radical adds on to the other nitrogen atom.

In aqueous media a ketone molecule is readily split off, and the resulting hydrazide is now benzylated at the amino-group instead of the carbamoyl group:



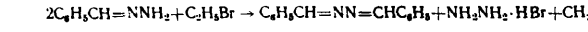
The yield of the 2,2-dibenzylhydrazide depends on the strength of the base used to combine with the hydrogen chloride liberated in the reaction. In the presence of pyridine a 14% yield of 1,1-dibenzyl-2-acetohydrazide is obtained, but with triethylamine the yield is increased to 50%. When, however, acetohydrazide is treated with benzyl chloride in aqueous sodium carbonate solution, the main product of the reaction is tetrabenzylhydrazine: *i.e.* under these conditions the acetyl group is eliminated as well.

The simplest alkyl halides do not react at their boiling points with the sodium enolate of acetone acetylhydrazone, and when reaction is carried out in an autoclave at 150°, monoalkylhydrazines are not formed, but mainly symmetrical dialkylhydrazines [36,109].

Alkylation of hydrazides themselves is less suitable for the preparation of monoalkylhydrazines, since alkylation takes place at the non-acylated nitrogen atom, both amino-hydrogen atoms being replaced [110-113]. A monoalkylhydrazide can be obtained and isolated only by the action of the alkyl halide on the sodium derivative of the hydrazide (formed by the action of metallic sodium in benzene) [114]:

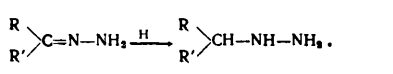
In the same way, cyanoethylation of hydrazides takes place at the NH_2 group, but in the presence of alkaline agents also at the NH group [78].

Attempts to alkylate non-acylated hydrazones with alkyl halides (which should give alkylhydrazines after hydrolysis of the alkylation products) give azines. For example, treatment of benzaldehyde hydrazone with ethyl bromide yields benzylidene azine [115]:

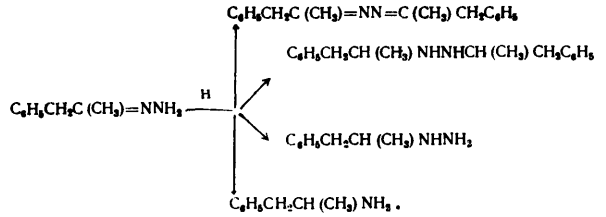


Sometimes, however, such alkylation can be carried out, for example in the case of acetone hydrazone [116].

Reduction of hydrazine derivatives. Many hydrazine derivatives containing a carbon–nitrogen double bond, which on reduction are converted into alkylhydrazines, have been tried. Thus hydrazones are reduced directly to monoalkylhydrazines:

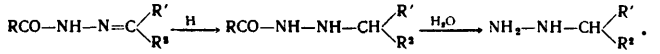


The reducing agents used have been sodium in alcohol [117,118], sodium amalgam [53,119-122], and lithium tetrahydroaluminate [123-125]. Catalytic hydrogenation has also been employed [126-129]. The N–N bond is sensitive to hydrogenation, and therefore the choice of reaction conditions is especially important in this last case for the successful preparation of alkylhydrazines. For example, hydrogenation of the hydrazone of benzyl methyl ketone can yield, depending on the conditions, four substances — the azine of this ketone, 1,2-bis-α-methylphenethylhydrazine, α-methylphenethylhydrazine, or α-methylphenethylamine [1]:



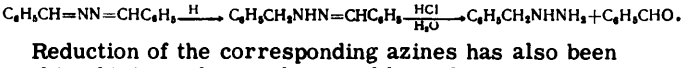
Platinum oxide or platinum on a carrier is usually employed as catalyst. Raney nickel is inconvenient, since it ruptures the N–N bond [130]. It must again be emphasised that the hydrogenation of hydrazones can yield alkylhydrazines only with a very delicate choice of conditions. Usually the N–N bond is broken with the formation of primary (and to some extent secondary) amines.

It is therefore preferable to reduce acylhydrazones instead of hydrazones themselves, since the N–N bond is rather more stable in the former. The resulting acyl derivatives can then be hydrolysed to the free monoalkylhydrazines:



The method of reduction most often used is hydrogenation of the acylhydrazones over a platinum catalyst (platinum oxide or platinum on a carrier) [2,126,131-145]. Raney nickel can also be used [116]. In several cases lithium tetrahydroaluminate has been employed [116,146,147]. It is true that in this case, depending on the nature of the initial acylhydrazone and the reaction conditions, reduction may go further, the corresponding 1,2-dialkylhydrazine being formed by reduction of the carbonyl group [147,148]. Nevertheless, predominant formation of 2-alkylhydrazides can be achieved, since the carbonyl group is more difficult to reduce [149,150].

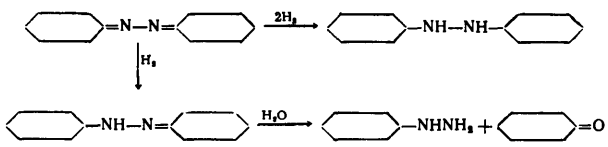
Aldazines and ketazines can be used as starting materials for the preparation of monoalkylhydrazines by reduction [30,117,151-156], although the C : N double bond in azines is fairly inert towards reduction [157,158]. Thus in 1900 Curtius [159] showed that, when benzylidene azine and its homologues are reduced in alkaline media (with sodium amalgam), one molecule of hydrogen is added, followed by a second molecule. In acid media (zinc dust in a mixture of acetic and hydrochloric acids), however, the N–N bond is broken with formation of mono- and di-benzylamines. Monoalkylhydrazines are obtained by hydrolysis of the products of the first stage in the reduction (with sodium amalgam), *i.e.* by hydrolysis of alkylhydrazones, an alkylhydrazine and a carbonyl compound being formed. In this way Wohl [160] and Curtius [159,161] synthesised benzylhydrazine from benzylidene azine:



Reduction of the corresponding azines has also been used to obtain nuclear-substituted benzylhydrazines, for example the 4-methyl, 2,4-dimethyl, and 2,4,5-trimethyl derivatives [159,162].

This process can be extended in only a limited degree to the purely aliphatic series, since aliphatic azines are considerably more resistant to reduction, as is confirmed by the work of Thiele [30], who was unable to reduce the azine of acetone electrolytically, although under these conditions benzylidene azine is reduced to 1,2-dibenzylhydrazine. On

the other hand, Kizhner[117] reduced cyclohexylidene azine with sodium in alcohol, and converted it into a mixture of cyclohexylhydrazine and 1,2-dicyclohexylhydrazine (he assumed that he had obtained the unsymmetrical derivative, the structure of his product being proved later[163]):

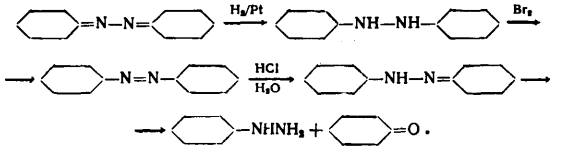


The azine of 3-methylcyclohexanone reacts similarly[164].

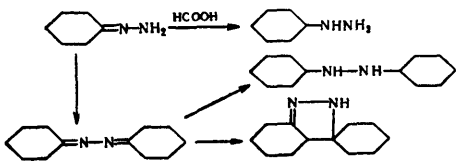
Taipale published a series of papers[152,165-169] on the hydrogenation of azines over platinum. In this case reaction takes place at normal temperatures with a slight excess pressure of hydrogen. If necessary, the process can be stopped after only one double bond has been hydrogenated, when alkylhydrazones of the corresponding aldehydes or ketones are obtained, hydrolysis of which can give alkylhydrazines, as shown above for benzylidene azine. However, this method was not adapted for preparative purposes.

Reduction of azines with lithium tetrahydroaluminate gave predominantly symmetrical dialkylhydrazines[155,170,171].

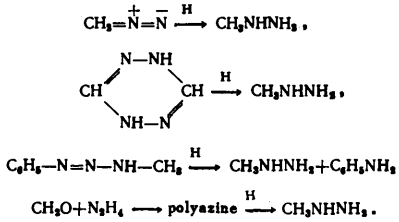
1,2-Dialkylhydrazines can be converted into monoalkylhydrazines by oxidation to the corresponding azo-compounds followed by hydrolysis with dilute mineral acid, which involves preliminary isomerisation to an alkylhydrazone. Harkins and Lochte[163] used this method to synthesise cyclohexylhydrazine from dicyclohexylhydrazine (obtained by catalytic hydrogenation of the azine of cyclohexanone over colloidal platinum):



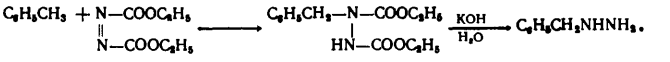
Cyclohexylhydrazine has been obtained in 31% yield also by the reduction of cyclohexanone hydrazone with anhydrous formic acid; 3,4-tetramethylene-5,5-pentamethylenepyrazoline and dicyclohexylhydrazine are also obtained, with the intermediate formation of cyclohexylidene azine[172]:



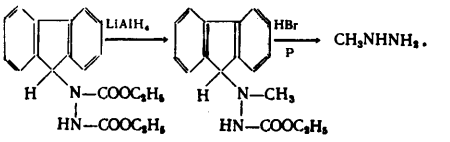
Finally, isolated reductions have been reported for the preparation of methylhydrazine – the reduction of diazomethane with sodium amalgam[173], of dihydrotetrazine with zinc and acetic acid[174], and of methylphenyltriazen[175] and the polymeric azine of formaldehyde with sodium amalgam[176]:



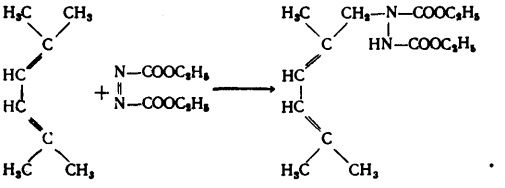
Syntheses with azocarboxylic ester. Azocarboxylic ester adds on various aromatic hydrocarbons containing alkyl radicals to form diethyl 1-aralkylhydrazine-1,2-dicarboxylates[150]. When the adducts are heated with methanolic caustic potash, aralkylhydrazines are obtained in yields up to 56% (based on the adduct, which in turn is formed in yields of 3–43% depending on the experimental conditions):



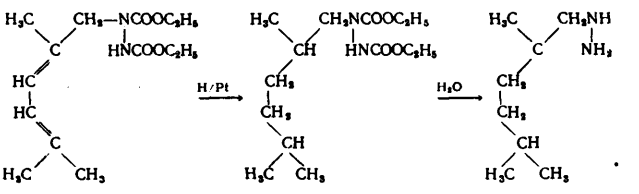
It is noteworthy that, on reduction with lithium tetrahydroaluminate, adducts of azocarboxylic ester and aromatic hydrocarbons are converted into ethyl 2-aralkyl-2-methylhydrazine-1-carboxylates, which on being heated with hydrobromic acid and red phosphorus break down with the formation of methylhydrazine, as has been shown in the case of the fluorene adduct[150]:



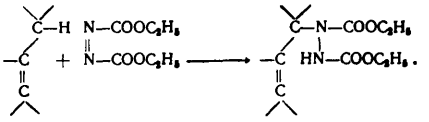
gem-Dialkylbutadienes react similarly to aromatic hydrocarbons with azocarboxylic ester; for example, 2,5-dimethylhexa-2,4-diene gives the corresponding adduct in 70–75% yield[177]:



These addition products had previously been regarded as diethyl 1,2,3,6-tetrahydropyridazine-1,2-dicarboxylates[178,179], since the reaction was assumed to follow the usual mechanism of diene synthesis. However, Levina *et al.* have shown[177] that it represents a substitutive addition. The double bonds in the adduct can be hydrogenated over a platinum catalyst in the cold, an alkylhydrazine being obtained after hydrolysis[177]:

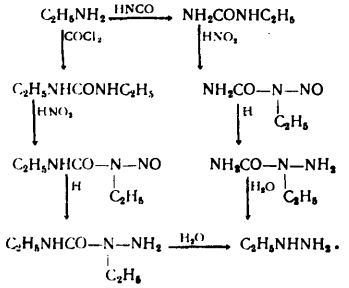


Azocarboxylic ester reacts not only with dienes but also with monoalkenes containing at least one hydrogen atom attached to an α-carbon atom [180-183], and this can also be used to obtain the corresponding alkylhydrazines:



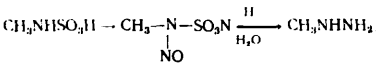
2. Synthesis Involving Formation of the N–N Bond

Nitrosation of an amino-group followed by reduction. The first information on monoalkylhydrazines was published as long ago as 1876 by Fischer [184], who found a route to their synthesis from primary amines *via* urea derivatives. Actually, reaction of nitrous acid with primary amines, which served as a method for the synthesis of arylhydrazines, was impossible with aliphatic amines because of rapid deamination. In order to avoid this, alkylamines are converted by means of cyanic acid or carbonyl chloride into mono- or di-alkylureas, which can now be nitrosated with nitrous acid. On careful reduction (with zinc and acetic acid) the nitroso-group is converted into a hydrazino-group. Acid hydrolysis yields alkylhydrazine, carbon dioxide, and alkylamine [185,186]:



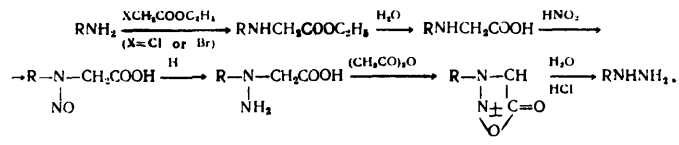
For a long time this classical method was the only one which could be considered for the preparation of alkylhydrazines, and was employed for the synthesis both of the simplest hydrazines (the methyl and ethyl derivatives [184,187]) and of more complicated products, for example hexamethylene-1,6-dihydrazine [44]. A substantial disadvantage of the method is the number of stages and the resulting low overall yield of monoalkylhydrazine.

Another method used to protect the amino-group before nitrosation was introduction of a sulpho-group. Thus nitrosation of methylsulphamic acid followed by reduction gave methylhydrazine [188]:

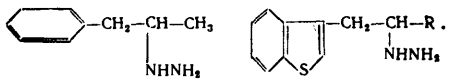


Alkylurethanes have been employed for the same purpose [189].

Finally, alkylhydrazines have been obtained during recent years by the acid hydrolysis of sydnones, which also are synthesised from primary amines [190-195]:

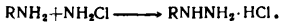


Originally used only in isolated cases, this method has subsequently been considerably extended, and can now be regarded as a fairly general procedure for the synthesis of monoalkylhydrazines [3,196-199]. It has been used in particular to synthesise α-methylphenethylhydrazine‡, which has an inhibiting effect on monoamine oxidase and is employed in the treatment of mental illness [3,198], and a series of 2-benzothienylethylhydrazines, which possess a hypotensive, analgesic, and sedative action [197]:



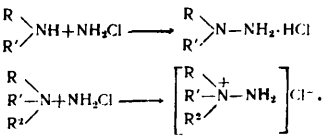
The reduction has also been reported of the comparatively stable nitramines for the preparation of methyl- and ethyl-hydrazines [200].

Reaction of amines with chloramine. A comparatively simple and extremely promising method developed in recent years for the synthesis of alkylhydrazines is based on the reaction of chloramine with primary amines [201-206]:



It is a modification of Raschig's well-known synthesis of hydrazine [207,208] from chloramine (hypochlorite and ammonia in the presence of aqueous alkali) and excess of ammonia.

The first paper on the use of Raschig's synthesis to obtain monoalkylhydrazines appeared in 1954 [201], when it was found that conditions for the preparation of methylhydrazine resembled in many respects those required for the synthesis of hydrazine itself (the addition of gelatin was needed, this being a deactivator of heavy metals; the alkalinity had to be maintained constant; etc.). The maximum yield of methylhydrazine was 64%. However, important differences were also found: firstly, the molar ratio of amine to chloramine required for the maximum yield of alkylhydrazine was considerably lower than that of ammonia to chloramine; and secondly, the temperature required for good yields of alkylhydrazines was considerably lower than was required for hydrazine. In the reaction of methylamine with chloramine, for example, considerable quantities of methylhydrazine are formed even at 0° and with a molar ratio of $CH_3NH_2 : NH_2Cl = 5$ (at room temperature, however, the process is complete in 20 min); whereas, if satisfactory yields of hydrazine are to be obtained, a molar ratio of $NH_3 : NH_2Cl = 20$ is necessary, and the ammonia–chloramine mixture must be heated to 60°. Subsequently, this method was extended to secondary and tertiary amines, and enabled unsymmetrical dialkylhydrazines [202-205,209] and tri-substituted hydrazinium salts [210-218] respectively to be obtained:



A useful improvement in the above method of obtaining alkylhydrazines is to carry out the reaction in the presence

‡ Obtained also by reduction of the hydrazone of benzyl methyl ketone [1].

of a tertiary amine, equivalent in amount to the free hydrazinium ions formed by the action of chloramine on the primary (or secondary) amine[205]. Addition of triethylamine in the preparation of methylhydrazine, for example, raises the yield of the latter from 55% to 75% (based on the chloramide).

There is also a reference in the patent literature to the production of alkylhydrazines by a process which is in some sense the opposite of the above method: amines are first converted into substituted chloramines, which then react with ammonia to form alkylhydrazines[219]:

$$RNHCl+NH_3 \longrightarrow RNHNH_2 \cdot HCl.$$

Thus this reaction represents ammonolysis of the chloramine.

Reaction of amines with hydroxylamine hydrogen sulphate. In 1925, long before Raschig's synthesis was extended to amines, several alkylhydrazines were produced in Germany by a similar method, in which the more complicated analogue of chloramine, hydroxylamine hydrogen sulphate, was employed[220,221]:

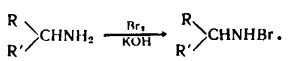
$$RNH_2+NH_2OSO_3H \longrightarrow RNHNH_2 \cdot H_2SO_4.$$

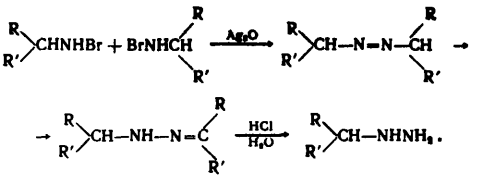
Under these conditions secondary amines give unsymmetrical dialkylhydrazines, and the reaction with tertiary amines yields quaternary 1,1,1-trialkylhydrazinium salts[222], so that the analogy with the Raschig synthesis is maintained in these cases too. For a long time this method failed to attract the attention of organic chemists, and it was only in 1949 that a second paper appeared on the use of this method to obtain a series of alkylhydrazines[223].

Recently a more detailed study of the reaction has been made by Gösl and Meuwsen[222,224], who found that better yields (up to 65%) of both mono- and di-alkylhydrazines are obtained in the presence of caustic potash, at elevated temperatures, and with molecular proportions of amine : NH_2OSO_3H : KOH = 2 : 1 : 2. Further increase in the proportion of amine produces only a slight increase in the yield of hydrazine. The presence of copper ions has a deleterious effect on the synthesis of monoalkylhydrazines. These workers consider that the production of hydrazines from amines and hydroxylamine hydrogen sulphate is to be regarded as a substitution, analogous to alkylation, for example methylation with dimethyl sulphate.

Hydroxylamine hydrogen sulphate itself is not produced in large quantities, which somewhat impedes widespread use of the method. The acid can be obtained from hydroxylamine sulphate and chlorosulphuric acid or oleum[220,225].

Action of silver oxide on bromamines. An interesting method for the synthesis of monosubstituted hydrazines was suggested by Kizhner[118,226-230]. The starting materials were primary amines in which the amino-group occupied a secondary position, and these were converted by the action of bromine and alkali into the corresponding bromamines. With silver oxide the latter gave azo-compounds, which immediately isomerised into hydrazones, on hydrolysis of which with hydrochloric acid the alkylhydrazines separated:



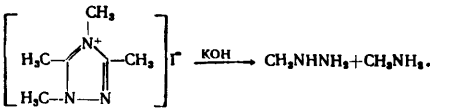


This method was employed by Kizhner for the preparation of hydrazines from 1-methylpentylamine, 1-propylbutylamine, 1-methylheptylamine, 3-methylcyclohexylamine, and *laevo*-menthylamine. However, this method is fairly complicated, and cannot be extended to the simplest radicals, since amines in which the amino-group occupies a primary position are oxidised by bromine to the corresponding nitriles.

3. Other Methods

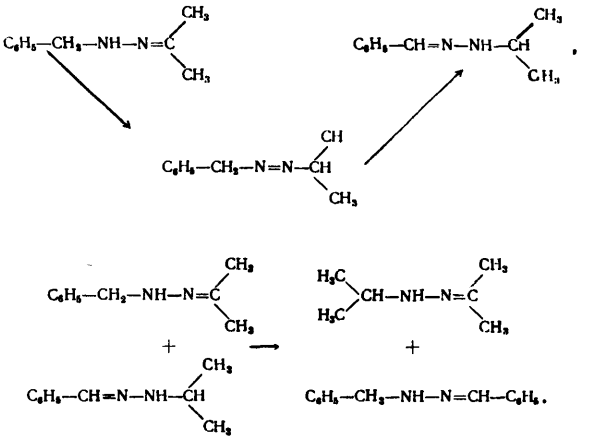
It has already been mentioned that symmetrical dialkylhydrazines can be converted into monoalkylhydrazines by oxidation to azo-compounds followed by hydrolysis[147]. The preparation of benzylhydrazine from the unsymmetrical dibenzylhydrazine by decomposition over a palladium catalyst has been described:

Methylhydrazine is obtained, together with methylamine, when 1,3,4,5-tetramethyl-1,2,4-triazolium iodide is heated in 50% caustic potash solution[232,233]:



It has also been reported that methylhydrazine is formed as a secondary product in the preparation of diazomethane from hydrazine and chloroform[234].

When acetone benzylhydrazone is heated with hydrogen chloride to 200°, acetone isopropylhydrazone is formed, together with hydrocarbons and pyrazole and pyrazoline bases. Probably the double bond first migrates to a conjugated position (decomposition of the intermediate azo-compound gives rise to the hydrocarbons), and then the two hydrazones undergo double decomposition[235]:



The benzaldehyde benzylhydrazone which is thus formed is unstable under the conditions of the reaction.

Several 2-hydrazinoethanols, on being heated to 200–215°, split off a molecule of methylhydrazine [236], the yields reaching 30%:

$$HO-\underset{R}{CH}-CH_2-NHNH_2 \longrightarrow O=\underset{R}{C}-H+CH_3-NHNH_2.$$

By analogy with Hofmann's method for the preparation of amines, substituted ureas could probably be converted by hypochlorites into the corresponding hydrazines:

$$R-NH-\overset{O}{\overset{\|}{C}}-NH_2 \longrightarrow R-NHNH_2.$$

This suggestion was made by Shestakov as long ago as 1903 [237], but has received no experimental confirmation.

III. PROPERTIES OF MONOALKYLHYDRAZINES

Among all the numerous class of monoalkylhydrazines and monoaralkylhydrazines, the properties of the two simplest members, methylhydrazine and benzylhydrazine respectively, have been most thoroughly investigated.

The lower monoalkylhydrazines are very hygroscopic, mobile, colourless liquids having a characteristic unpleasant odour, soluble in water, alcohol, and ether, and unstable in air. Much heat is evolved when they are mixed with water, and, like hydrazine itself, they can be freed from the latter only with difficulty. The boiling points of the first two members of the homologous series (methylhydrazine and ethylhydrazine) are lower than that of hydrazine itself. Like hydrazine, they are strong bases, but no quantitative estimate of the basic strengths of the alkylhydrazines has been made. It is only recently that the dissociation constants of some of the simplest hydrazines, including the methyl and ethyl derivatives, have been determined by potentiometric titration [238].

The simplest aralkylhydrazines (benzylhydrazine and phenethylhydrazine) possess similar properties [33,160].

The free bases of the higher alkylhydrazines are quite stable. From C_{12} they are solid at room temperature. Since they are strong bases, they absorb carbon dioxide, forming carbonates [18].

With acids, alkylhydrazines can give two series of salts, acid and normal. The former are obtained by reaction of the bases with excess of acid, and the latter by dissolving the acid salts in water and evaporating the solutions. The acid sulphates, oxalates, and picrates usually crystallise well. Hydrochlorides of the lower monoalkylhydrazines are extremely hygroscopic, and have no definite melting points. Those of the aralkylhydrazines are obtained in crystalline form without great difficulty.

The free bases are obtained from the salts by repeated distillation with concentrated and solid alkali or even with barium oxide [11,160,185,187]. There is also an indication of the possibility of isolating the base from methylhydrazine sulphate by the action of liquid ammonia [239].

Alkylhydrazines are extremely corrosive substances, strongly attacking skin, rubber, corks, and even glass to some extent [187]. Data have been published [240] on the infrared spectrum of methylhydrazine.

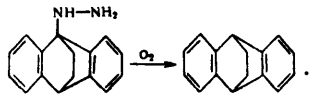
The lower alkylhydrazines are extremely toxic. Thus even at a concentration of 0.01%, methylhydrazine in the form of the free base destroys the lower forms of animal life, bacteria, and fungi [241].

Oxidation and Reduction

Like hydrazine itself, alkylhydrazines are readily oxidised, and immediately reduce Fehling's solution and ammoniacal silver oxide, nitrogen being evolved and the corresponding hydrocarbon being formed [11,185,187]:

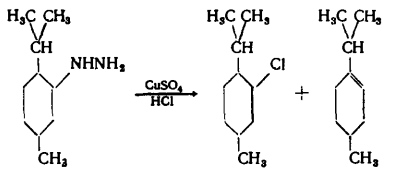
$$RNHNH_2 \xrightarrow{O} RH+N_2+H_2O.$$

Sometimes oxidation in air occurs so readily that the free base cannot be isolated at all from the salt, as has been shown in the case of 9-hydrazino-9,10-dihydro-9,10-ethanoanthracene [195]:



The oxidative breakdown of aralkylhydrazines of this type involves free radicals [242].

Potassium ferricyanide effects especially smooth oxidation of alkyl- and cycloalkyl-hydrazines [118]. An attempt to effect the autoxidation of menthylhydrazine by means of copper sulphate in hydrochloric acid medium gave a mixture of menthene and menthyl chloride [243]:



Wohl and Oesterlin [160] oxidised benzylhydrazine with ferric chloride in acid medium, and obtained benzylidene azine and a salt of hydrazine. The primary process probably consists in the formation of benzaldehyde hydrazone, which then undergoes disproportionation:

$$C_6H_5CH_2NHNH_2 \xrightarrow{O} C_6H_5CH=N-NH_2 \xrightarrow{HCl} C_6H_5CH=N-N=CHC_6H_5 + NH_2NH_2 \cdot HCl.$$

9-Hydrazino-9-phenylfluorene on oxidation has also been converted into the corresponding azo-compound [27].

The oxidation of monoalkylhydrazines has been used for their quantitative determination [244,245].

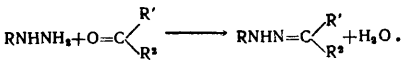
Monoalkylhydrazines are not reduced by mild reducing agents. Under severe conditions, for example catalytic hydrogenation over Raney nickel, however, the N–N bond undergoes hydrogenolysis. This reaction was studied by Hinman [146,147,246], which enabled it to be used subsequently even for the preparation of some primary and secondary amines [1]:

$$C_6H_5CH_2-\underset{CH_3}{CH}-NHNH_2 \xrightarrow[Ni/R]{H} C_6H_5CH_2-\underset{CH_3}{CH}-NH_2+NH_3,$$

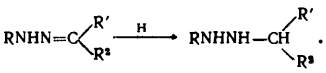
$$(C_6H_5CH_2)_2NNH_2 \xrightarrow[Ni/R]{H} (C_6H_5CH_2)_2NH+NH_3.$$

Reactions Involving the NH_2 Group

Alkylhydrazines react with aldehydes and ketones (including sugars) to form the corresponding alkylhydrazones [12,20,33,60,115,159,160,194,234,247-251]:

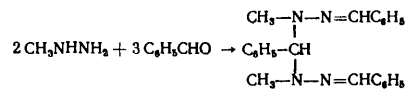


Reduction of alkylhydrazones can be used for the preparation of 1,2-dialkylhydrazones [252-256]:

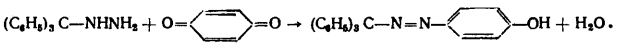


Attempts to employ alkyl- or aralkyl-hydrazines for the identification of carbonyl compounds were made long ago by Fischer, but most of the hydrazones obtained were liquid or did not crystallise readily.

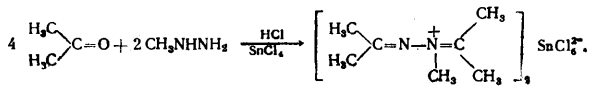
Sometimes the reaction between an alkylhydrazine and a carbonyl group takes an unusual course. Thus methylhydrazine, which gives a hydrazone of normal structure on treatment with an equimolecular quantity of benzaldehyde, forms "tribenzylidenemethylhydrazine" with excess of benzaldehyde [20]:



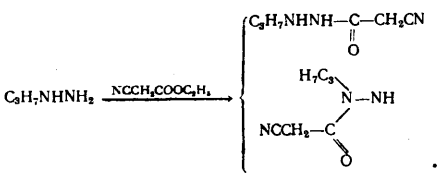
Triphenylmethylhydrazine and *p*-benzoquinone form not a hydrazone but *p*-triphenylmethylazophenol [26]:



In the presence of tin(IV) chloride and hydrochloric acid, methylhydrazine gives with many aldehydes and ketones crystalline *N*-methylketazinium and *N*-methylaldazinium hexachlorostannates [257,258]:

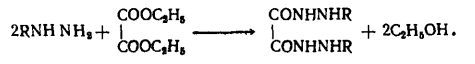


Alkylhydrazines undergo acylation at either the NH or the NH_2 group depending on the reagent and the reaction conditions. With mild acylating agents, for example esters, alkylhydrazines are monoacylated at the NH_2 group [125,259-262]. Depending on the temperature, propylhydrazine gives with ethyl cyanoacetate either a symmetrically substituted (on cooling) or an unsymmetrically substituted (on heating) *N*-propylcyanoacetohydrazide [259]:

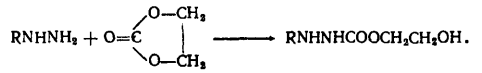


Alkylhydrazines which have been acylated with isonicotinic acid possess antitubercular activity [132,133,262-264] (see p. 171). The analogous products obtained with nicotinic acid have an antidepressive action [265].

Alkylhydrazines react in the normal manner with esters of dibasic acids, oxalic ester, for example, yielding *N*-alkyloxalohydrazides [33,185,187], in which the NH_2 group has been acylated:



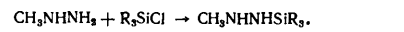
Equimolecular quantities of ethylene carbonate and alkylhydrazines form 2-hydroxyethyl alkylhydrazinecarboxylates [266]:



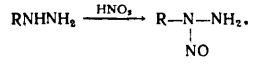
Acylation of the NH group is discussed below.

Reactions Involving the NH Group

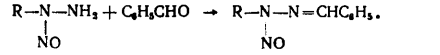
As already mentioned (see p. 160), alkylhydrazines undergo alkylation with alkyl halides at the substituted nitrogen atom (if this is not prevented by steric factors), with the successive formation of 1,1-dialkylhydrazines and trialkylhydrazinium salts [13,18-20]. When the alkyl halide contains a bulky radical, 1,2-dialkylhydrazines are obtained [267-269]. With a trialkylsilyl chloride, too, alkylhydrazines react at the NH_2 group [270]:



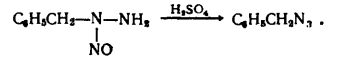
With nitrous acid, alkylhydrazines form nitroso-derivatives [11,30,119,160,194,271]:



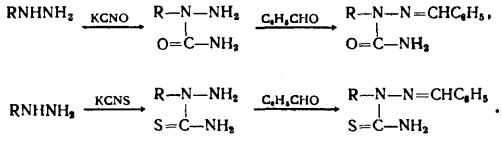
Alkylnitrosohydrazines are relatively stable, colourless, crystalline substances, and give a characteristic violet coloration with ferric chloride. The position of the nitroso-group is established by the fact that they give hydrazones with aldehydes, and therefore contain a free amino-group [11,119]:



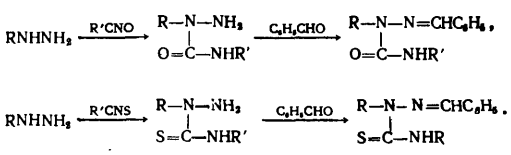
Benzylnitrosohydrazine is converted by dilute sulphuric acid into benzyl azide [119]:



Treatment of the salts of alkylhydrazines with potassium cyanate and thiocyanate gives respectively alkylsemicarbazides and alkylthiosemicarbazides, which yield the corresponding alkylsemicarbazones with aldehydes and ketones [32,185,187,223,272,273]:

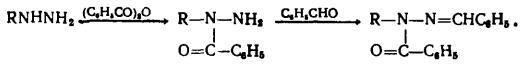


Similar reactions occur between alkylhydrazines and esters of isocyanic and isothiocyanic acids [32,185,187,272-279]:



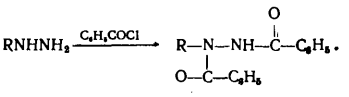
These reactions take place readily at room temperature, and thus there is no necessity to heat in order to speed them up [33].

Acylation of alkylhydrazines with the calculated quantity of acid anhydrides yields monoacyl derivatives in which the secondary nitrogen atom has been acylated, as can yet again be proved by the formation of hydrazones with benzaldehyde [78,273]:



Sometimes such acylation can be effected with esters and even with the acids themselves [259-261].

If acylation is carried out more rigorously, for example with acid halides by the Schotten–Baumann method or by heating with excess of the acid anhydride, the reaction can go further and affect the NH_2 group, with formation of diacyl derivatives [33,67,139,159]:

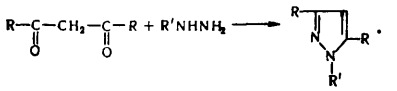


This last reaction is employed for the identification of alkylhydrazines.

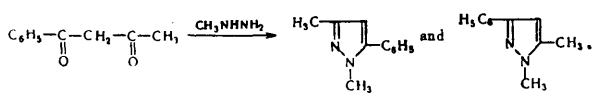
Reactions Involving Both Nitrogen Atoms

Reactions in which both nitrogen atoms of an alkylhydrazine take part usually result in heterocyclic compounds. They occur in the same way as with hydrazine itself, but the corresponding *N*-alkyl derivatives are obtained.

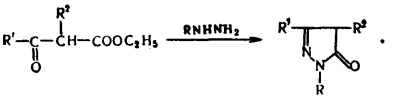
Reaction of alkylhydrazines with 1,3-difunctional compounds yields pyrazole derivatives. From 1,3-diketones or the corresponding acetals are obtained 1-alkylpyrazoles [280-290]:



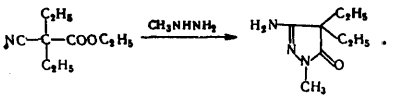
Unsymmetrical diketones give two isomeric pyrazoles with alkylhydrazines. Thus 1-phenylbutane-1,3-dione reacts with methylhydrazine to form 1,3-dimethyl-5-phenylpyrazole and 1,5-dimethyl-3-phenylpyrazole in the ratio 1 : 3: [291]



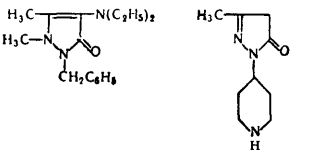
Similarly, acetoacetic ester and its homologues with alkylhydrazines yield 1-alkylpyrazol-5-ones [35,75,161,281,292-303]:



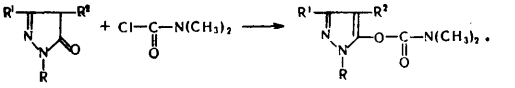
The corresponding aminopyrazolones are obtained from methylhydrazine and cyanoacetic or ethylcyanoacetic esters [300,304,305]:



Several of these pyrazolones, for example 1-benzyl-2,3-dimethyl-4-diethylaminopyrazol-5-one and 3-methyl-1-piperid-4′-ylpyrazol-5-one, exert an analgesic, antipyretic, spasmolytic, or antihistaminic action [296,297,303]:



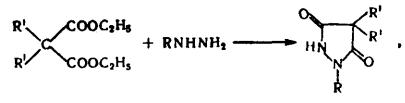
The 1-alkylpyrazolones obtained in this way are converted by dimethylcarbamoyl chloride into pyrazolyl dimethylcarbamates, which exert a strong anti-cholinesterase action [109,303-308]:



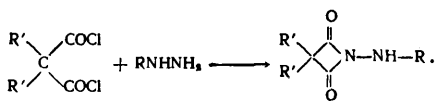
In particular, a compound of this type is used under the name "Isolan" [R = $(CH_3)_2CH$, $R^1 = CH_3$, $R^2 = H$] as a systemic insecticide for the control of suctorial insect pests of plants [307-309]. The preparation Indasol (R = $CNCH_2CH_2$, $R^1 = CH_3$, $R^2 = H$) is an efficient aphicide, and is less toxic to warm-blooded animals than is Isolan [109,306].

Pyrazolone dyes have also been described, obtained by coupling 1-alkylpyrazolones with various aromatic diazo-compounds [75,295,310,311].

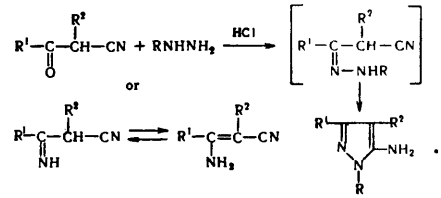
With substituted malonic esters, alkylhydrazines give pyrazolidinediones [312-315]:



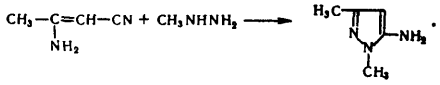
azetidine-2,4-dione being formed as a byproduct [312,315]. The latter can be obtained as the main product by treating the monoalkylhydrazine with a disubstituted malonyl chloride [316]:



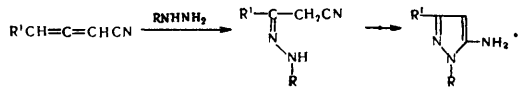
Aminopyrazole derivatives are obtained by the reaction of alkylhydrazines with malononitrile or its dimer [317], with ethoxymethylenemalononitrile and its homologues [317-319], and with α-cyano-β-ethoxyacrylic ester [6,318,320]. The most convenient method for obtaining 5-aminopyrazoles is reaction of alkylhydrazines with β-keto- or β-amino-nitriles [321,322]:



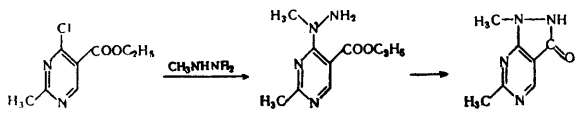
Thus, for example, a 97% yield of 1,3-dimethylpyrazol-5-amine has been obtained from methylhydrazine and the dimer of acetonitrile (β-aminocrotononitrile) [290,317]:



Pyrazolamines are formed also by the action of monoalkylhydrazines on 1-cyanoalka-1,2-dienes (cyanoallenes) [323]:

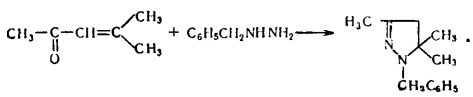


Fused ring systems containing a pyrazole ring, for example pyrazolopyrimidines, can be obtained by the condensation of monoalkylhydrazines with more complicated cyanides. With 4-chloro-5-cyano-2-dimethylaminopyrimidine, for example, isopropylhydrazine forms 3-amino-6-dimethylamino-2-isopropylpyrazolo[3,4-*d*]pyrimidine [6]. Similarly, the action of methylhydrazine on methyl 4-chloro-2-methylpyrimidine-5-carboxylate produces 1,6-dimethyl-3-oxopyrazolo[3,4-*d*]pyrimidine, in which case it is possible to isolate the primary product formed by replacement of the halogen by the hydrazino-group [324]:

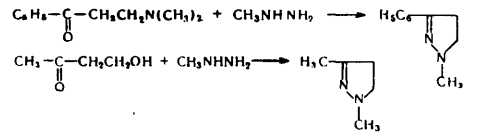


A series of such pyrazolopyrimidines have been synthesised recently, since among them have been discovered substances which possess an anticancer effect, as well as a stimulating action on the heart [6,318,320].

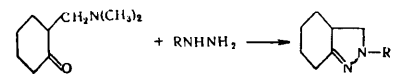
$\alpha\beta$-Unsaturated aldehydes and ketones react with monoalkylhydrazines to form 1-alkyl-Δ^2-pyrazolines [235,282,325-330]. For example, mesityl oxide reacts with benzylhydrazine to give 1-benzyl-3,5,5-trimethylpyrazoline [326]:



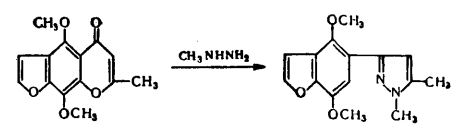
Pyrazolines are obtained also by the reaction of alkylhydrazines with several amino- and hydroxy-ketones. Thus 2-dimethylaminoethyl phenyl ketone [331] and 4-hydroxybutan-2-one [282] gave the corresponding pyrazolines with methylhydrazine:



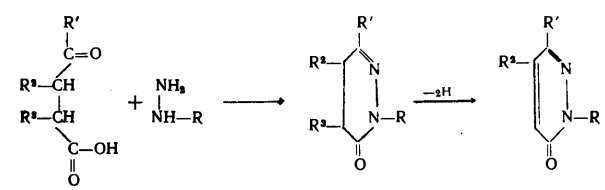
2-Dimethylaminomethylcyclohexanone forms, with methyl- and benzyl-hydrazines, pyrazolines which are substituted derivatives of hydrogenated indazoles [280]:



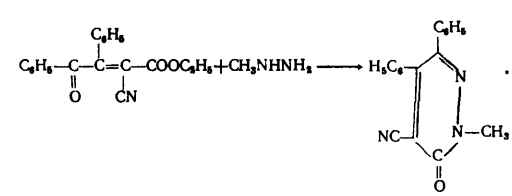
Alkylhydrazines, like phenylhydrazine and hydrazine itself, effect cleavage of the ring in several heterocyclic ketones, with subsequent formation of a pyrazole ring. Thus heating kellin with methylhydrazine opens the γ-pyrone ring and converts the compound into a pyrazolylbenzofuran [332]:



Condensation of γ-keto-acids or their reactive derivatives with monoalkylhydrazines gives 2,3,4,5-tetrahydro-3-oxopyridazines, which are readily dehydrogenated to the corresponding 2,3-dihydro-3-oxopyridazines [315,333]:

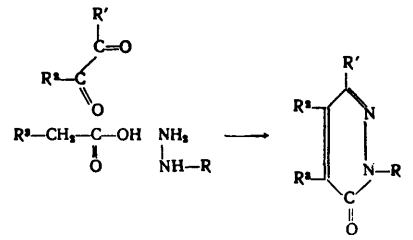


The latter compounds can be synthesised without a stage involving dehydrogenation if the corresponding unsaturated acid is used as starting material. For example, ethyl α-cyano-γ-oxo-$\beta\gamma$-diphenylcrotonate and methylhydrazine give 4-cyano-2,3-dihydro-2-methyl-3-oxo-5,6-diphenylpyridazine [334]:

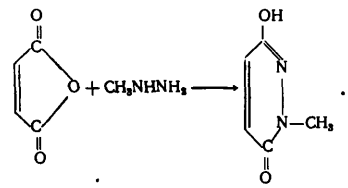


The method of Schmidt and Druey [335,336] effects in one stage the condensation of three components — a monoalkylhydrazine, an $\alpha\beta$-dicarbonyl compound or a reactive deri-

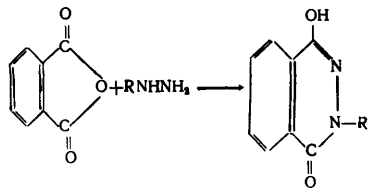
vative thereof, and an acid containing an α-methylene group or a reactive functional derivative thereof:



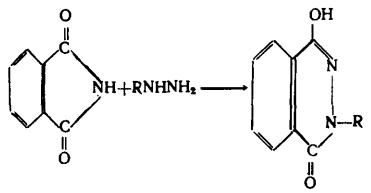
Dihydrohydroxyoxopyridazines can be obtained by the interaction of maleic anhydride and monoalkylhydrazines. Thus methylhydrazine yields 2,3-dihydro-6-hydroxy-2--methyl-3-oxopyridazine [337]:



Other alkylhydrazines react similarly [338,339]. On being heated with phthalic anhydride, monoalkylhydrazines form the corresponding hydroxyoxophthalazines [339-342]:



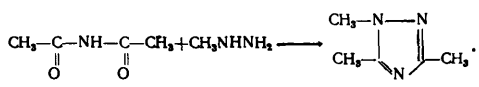
Phthalimide reacts similarly [341,343-347]:



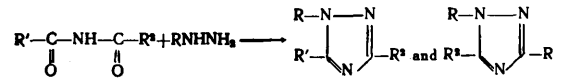
There are a fair number of publications in this field, since several pyridazine derivatives, for example 4-cyano-2,3--dihydro-2-methyl-3-oxo-5,6-diphenylpyridazine, possess analgesic and antipyretic properties [312,313,333,334,336].

1-Alkyl-4,5-dichlorodihydro-3-oxopyridazines have been patented as bacteriostatic and fungistatic compounds [348].

Condensation of monoalkylhydrazines with diacylamines, which represents a particular case of the Einhorn–Brunner reaction, results in substituted 1,2,4-triazoles [349-351]. For example, diacetimide and methylhydrazine yield 1,3,5-trimethyl-1,2,4-triazole [350]:



If the imide contains different acyl groups, the reaction gives a mixture of two isomeric triazoles [349]:



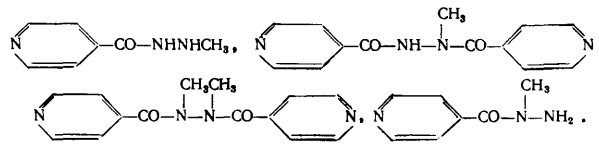
IV. BIOLOGICAL PROPERTIES OF ALKYL- AND ARALKYL-HYDRAZINES

As already mentioned, the lower monoalkylhydrazines are poisonous [241]. It has even been suggested [352] that research has been restricted by their toxicity. The higher alkylhydrazines, however, are far less toxic, and often have valuable pharmacological properties.

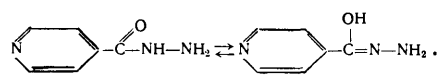
In view of the high antitubercular activity of the hydrazide of isonicotinic acid, many of its derivatives have been studied, as well as the hydrazides of other acids [132-134,262-264,353]. Since alkylidene and aralkylidene derivatives of isonicotinohydrazide possess high antitubercular activity, it has been suggested that such activity is due to their hydrolysis at the C : N bond, with formation of the above hydrazide in the organism [132]. In order to check this hypothesis, a series of 2-alkylhydrazides of isonicotinic acid having the general formula $4\text{-}C_5H_4NCONHNHR$ were synthesised, in which R represented CH_3, C_2H_5, C_3H_7, iso-C_3H_7, C_4H_9, iso-C_4H_9, C_6H_{13}, C_7H_{15}, C_8H_{17}, cyclohexyl, 4-methylcyclohexyl, 3-methylcyclohexyl, sorbit-1-yl, $C_6H_5CH_2$, p-$CH_3OC_6H_4CH_2$, $C_6H_5CH(CH_3)$, and $C_6H_5CH_2CH_2CH_2$. All of these compounds showed high antitubercular activity *in vivo* [132].

The analogous derivatives of nicotinic acid have an antidepressive effect [265].

It is interesting that the antitubercular activity of isonicotinohydrazide derivatives disappears when all the hydrogen atoms in the hydrazino-group have been replaced. Thus the methylhydrazides containing one and two isonicotinoyl groups exhibit antitubercular activity, whereas this is no longer present in 1,2-diisonicotinoyl-1,2-dimethylhydrazine. The 1-methylhydrazide of isonicotinic acid [262] and isonicotinoyl derivatives of various pyrazolines [354,355] are also inactive.



Thus the presence of an amide hydrogen atom is probably necessary for the appearance of antitubercular activity. This supports the hypothesis that such activity in isonicotinohydrazide is linked with the ability of the latter to pass into a pseudo-acid, which can form metal complexes [262]:

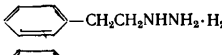


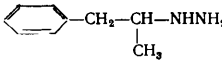
In the treatment of pulmonary tuberculosis with isonicotinohydrazide (Isoniazid) [356] it has been found that patients not only increase in weight but also overcome their state of depression and are in good spirits. The

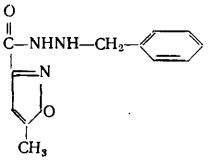
effect of the corresponding isopropylhydrazide (Marsilid) on the psychology of the patient is still more marked§. An intensive study has therefore been made of the psychopharmacological properties of various alkyl- and aralkyl--hydrazines and their acyl derivatives [1-3,49,100,123,128,129,143,145,198,253,268,357-368]. The antidepressant action of these compounds is due to suppression of the enzyne monoamine oxidase, which increases the concentration of serotonin in the human brain [357].

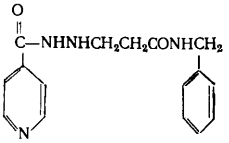
Hydrazines containing an α-methylphenethyl group have been proved to be good inhibitors of monoamine oxidase [1]. Such aralkylhydrazines are stronger inhibitors than the corresponding amines, their effect lasts longer, and they lower the blood pressure [1,362]. Substitution in the phenyl group, hydrogenation of the latter, alkylation or acylation at the nitrogen atoms, or replacement of phenyl by a heterocyclic radical produces a sharp fall in inhibiting activity.

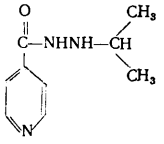
At the present time the following alkyl- and aralkyl--hydrazines are manufactured as monoamine oxidase inhibitors in various countries, and are employed for the treatment of mental illness [363]:


Phenethylhydrazine sulphate, phenelzine sulphate, Nardil


α-Methylphenethylhydrazine hydrochloride, Catron


2-Benzylhydrazide of 5-methylisoxazole-3--carboxylic acid, isocarboxazid, Marplan


2-Benzylcarbamoylethylhydrazide of pyridine-4--carboxylic acid, nialamide, Niamid


2-Isopropylhydrazide of pyridine-4-carboxylic acid, iproniazid phosphate, Marsilid

Various qualitative colour reactions have been worked out for all these preparations [363].

Among aralkylhydrazines have been found substances which resemble oxytocin in stimulating the smooth muscle of the uterus [7-9]. Thus benzylhydrazine and 2,5-dimethoxybenzylhydrazine hydrochlorides increase the duration of the spontaneous uterine contractions without changing their strength or tone. 3,4-Dimethoxybenzylhydrazine hydrochloride (Vetrazin), which has been developed by the present reviewers, is a strong stimulant of labour even at a dilution of 1 : 1 000 000 (in doses of 0.5–5 mg kg^{-1}).

During recent years many alkyl- and aralkyl-hydrazines and their simple derivatives have been patented as possessing a hypotensive, sedative, analgesic, local anaesthetic, spasmolytic, antirheumatic, or antiblastomic action [144,162,197,206,247,249,267].

§ Marsilid is no longer employed as an antitubercular remedy [356].

Finally, alkylhydrazines are widely used as intermediates in the synthesis of more complicated medicinals [6,116,219,250,296,297,303,312,313,315,318,320,333,335,336].

In the present review we have not discussed the chemistry of di-, tri-, and tetra-alkylhydrazines. Several methods for synthesising these substances are similar to those used for the preparation of monoalkylhydrazines, but the most important are specific to these structures. The differences in chemical reactions between mono- and poly--alkylhydrazines are still greater. The literature on these compounds, especially on dialkylhydrazines, is fairly extensive, so that it cannot be covered within the present review.

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HEXACHLOROBUTADIENE

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1. INTRODUCTION

Replacement of all the hydrogen atoms in the butadiene (divinyl) molecule by chlorine atoms produces the comparatively little known compound hexachlorobuta-1,3-diene, a colourless liquid with an odour of turpentine.

Hexachlorobutadiene was first described in 1893 by Besson[1], who separated it from the thermal conversion product of chloroform. Unlike butadiene, hexachlorobutadiene is comparatively inert chemically and has a number of unexpected properties; it was these which made its identification difficult and produced several conflicting reports of its chemical properties.

There are reports[2-4] that hexachlorobutadiene is formed in the chlorination of hydrocarbons and their halogen derivatives under pressure, but Fruhwirth showed[5] that the compound so obtained is octachlorocyclopentene. The opposite mistake has also been made. In the chlorination of 1,3-dichlorobut-2-ene Akopyan *et al.*[6] isolated a substance which they could not identify, and which Jelinek and Hudlicky[7] showed to be hexachlorobuta-1,3-diene.

Hexachlorobutadiene behaves as though fully saturated[5]: it does not add chlorine in sunlight, does not react in the Diels–Alder reaction, is stable to acids and alkalis, unlike other highly chlorinated unsaturated compounds it does not give carboxylic acids with concentrated sulphuric acid, and it does not react with sulphuryl chloride in the presence of benzoyl peroxide[8]. More recent studies have only refined our knowledge of these properties of hexachlorobutadiene.

For a long period this compound had remained little known, and only recently has it begun to take on practical value[9].

2. PHYSICAL PROPERTIES

Hexachlorobutadiene is a colourless liquid with an odour of camphor[10]; it has the following physical properties: b.p. 215°/760 mmHg,[5] m.p. 18.6°,[10] n_D^{20} 1.5557,[10] d_4^{20} 1.6794,[10] molar volume at absolute zero 133 ml,[11] molar refraction (excluding the exaltation of the conjugated bonds) 48.94.[5] Its vapour pressure is 100 mmHg at 142–144°, 50 mmHg at 123°, and 20 mmHg at 101°.[12] It has zero dipole moment[13]. Its dielectric constant at 20° is 2.55,[11,13] and its breakdown potential has been reported as 194,[14] 200,[15] and 890 kV cm^{-1}.[16]. The large variation in these values is possibly due to the difference in purity of the actual samples. The molecular polarisation is 52.8 cm^3 and, as expected from the zero dipole moment, is independent of temperature.

The viscosity is 2.446 cP at 37.8° and 1.31 cP at 98.9°.[8] In the interval 50–90° the viscosity is described by the equation[11,16] $\ln\eta = A + Q/RT$, where Q is the energy of activation for the transfer of a particle of the liquid from one equilibrium position to a neighbouring equilibrium position in the same liquid. The surface tension at 20° at the interface with air is 35.9 dyn cm^{-1}.[17] The angle of contact of hexachlorobutadiene on various surfaces has been given by Zisman and coworkers[18-20].

Roedig and Kloss[12] determined the ultraviolet spectrum, Szasz and Sheppard[23] the infrared spectrum, Kohlrausch and Wittek[24] and Batuev and Matveeva[25,26] the Raman spectrum of hexachlorobutadiene; it was concluded that the hexachlorobutadiene molecule does not have the *trans*-configuration, and Kohlrausch and Wittek also excluded the possibility of a planar *cis*-configuration, since such a structure would have a distance between the extreme chlorine atoms of 1.7 Å, *i.e.* less than the bond length in the chlorine molecule (1.98 Å). It was therefore assumed that the hexachlorobutadiene molecule is non-planar, probably with one half of the molecule twisted relative to the other half so that the position of the molecule as a whole corresponds to the minimum potential energy allowing for the repulsion of the chlorine atoms.

On the basis of their investigation of hexachlorobutadiene at low temperatures, Szasz and Sheppard exclude the possibility of a mixture of non-planar rotational isomers. They suppose that two pairs of different minima on the potential energy curve for rotation about the C–C bond are possible; these minima must lie between the maxima corresponding to the unstable *cis*- and *trans*-positions and between the 90° maxima corresponding to the least favourable overlap of the π electrons of the two double bonds of the molecule. The preponderance of a single rotational isomer demonstrates that either one of these minima is considerably lower than the other, or the steric effects are so large that there is a single pair of minima near the 90° position. This last type of configuration was suggested by Kohlrausch and Wittek and confirmed by Szasz and Sheppard.

The lifetime of the phosphorescent triplet state of hexachlorobutadiene varies from 1 to 10 s.[27] The energy of the triplet state allowing for the zero point energy of the molecule is 75 kcal.

The physical properties of mixtures of hexachlorobutadiene with other compounds have been little studied. The freezing point of hexachlorobutadiene is lowered when hexachloropropylene is added to it[28].

Study has been made[11] of certain physical properties of a mixture of hexachlorobutadiene with a paraffin-base mineral oil (molecular weight 263, d_4^{20} = 0.8825): with increasing temperature the volume increases, with a maximum with an equimolar mixture, and the volume difference increases.

The molar polarisation of a mixture of hexachlorobutadiene with a mineral oil (of dielectric constant 2.215 D and molar polarisation 86 cm^3) increases linearly with the oil content of the mixture, indicating that the change of volume, referred to above, when the liquids are mixed must be considered an effect due to packing of the molecules of the two liquids.

The variation of viscosity with the composition of the mixture has been investigated (Fig. 1). The deviation of the plot $\log\eta = f(n)$, where n is the molar content of oil in the mixture, from a straight line demonstrates the existence of intermolecular interaction between the two compounds. Berger and Joerges[11] determined the difference between the experimental value of $\ln\eta$ and that calculated from the equation $\ln\eta = A + Q/RT$;[16] the difference is positive and depends on the quantity of heat ΔQ additional to the energy of activation which is liberated by the mixing of the two liquids. At low temperatures this value is within the limits of the experimental error. For 60° and 90° and an equimolecular mixture, ΔQ is 40 and 60 kcal respectively.

Ellison and Zisman[17] studied the decrease in the surface tension of a solution of the highly fluorinated nonyl

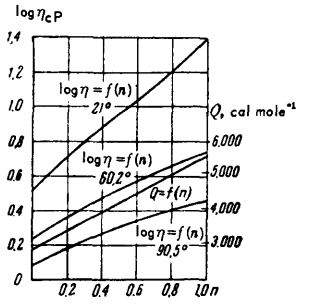


Fig.1. Logarithm of the viscosity and the energy of activation of a mixture of hexachlorobutadiene and mineral oil as functions of the composition of the mixtures. Q is the value for temperatures of 60-90°.

butyrate $H(CF_2)_3COOCH_2(CF_2)_6H$ in hexachlorobutadiene as the concentration of the solution was increased, and found the surface activity to increase exponentially with the difference between the surface tensions of the solution and the pure ester.

Strigel[14] determined the impulse coefficient and other electrical properties of mixtures of hexachlorobutadiene with transformer oil, and showed that the breakdown potential of a mixture containing 3% hexachlorobutadiene is 125 kV cm^{-1}, while for pure hexachlorobutadiene and mineral oil it is 194 and 154 kV cm^{-1}.

The solubility of chlorine and carbon dioxide in hexachlorobutadiene has been studied[29].

3. CHEMICAL PROPERTIES

Reactions

Fruhwirth first studied the chemical properties of hexachlorobutadiene, and showed[5] that reduction with nascent hydrogen produces butadiene.

Zinc dust in boiling alcohol reduces hexachlorobutadiene to diacetylene in 25% yield[30].

It can be assumed that the reduction of hexachlorobutadiene proceeds in stages:

$$CCl_2{=}CCl{-}CCl{=}CCl_2 \rightarrow CH{\equiv}C{-}C{\equiv}CH \rightarrow CH_2{=}CH{-}C{\equiv}CH \rightarrow CH_2{=}CH{-}CH{=}CH_2.$$

Reduction of hexachlorobutadiene with deuterium oxide and zinc produces fully deuterated butadiene[30-32].

Prolonged bubbling of oxygen containing 1% chlorine through hexachlorobutadiene at 165-180° converts half of the reactant into various oxygen-containing compounds, of which the main product is CCl_3COCCl_2COCl.[33]

Hexachlorobutadiene does not react with chlorine when passed through an empty tube at 500°,[34] but passage of a mixture of chlorine and hexachlorobutadiene through a tube of diatomite at 450° produces decomposition of 15-20% of the initial reactant[34,35].

Hexachlorobutadiene is not chlorinated in the light but irradiation of the mixture in a sealed tube at above 25° produces hexachloroethane[8]. Somewhat later[34] prolonged action of chlorine on hexachlorobutadiene in bright sunlight at 10-20° also was found to give hexachloroethane in almost quantitative yield.

The destructive chlorination of hexachlorobutadiene in light is accelerated by ferric chloride[36]; reaction is then marked even at 0°.

It is clear that the addition of chlorine to the double bonds of hexachlorobutadiene is very difficult to accomplish, and this was confirmed by McBee and Hatton[8], who attempted unsuccessfully to carry out the reaction in a sealed tube in light at temperatures of from -70° to 75°, and by Roedig[36], who was unable to add gaseous chlorine to hexachlorobutadiene at temperatures up to 200°. However, prolonged keeping of a mixture of hexachlorobutadiene and liquid chlorine in sealed ampoules in daylight did produce addition of chlorine to the double bonds[36], the main products being octachlorobutene or decachlorobutane depending on the molar ratio of reactants used.

Fluorination of hexachlorobutadiene is accomplished comparatively readily, and this has been its most studied reaction. Different polychlorofluorobutanes and polychlorofluorobutenes are obtained by using different fluorinating agents, such as fluorine[37,39], hydrogen fluoride[39-41], chlorine trifluoride[42-44], and selenium tetrafluoride[45], with catalysts such as antimony trichloride, antimony pentafluoride, and lead peroxide, and carrying out the reaction in the liquid or gaseous phase.

The fluorination of hexachlorobutadiene with hydrogen fluoride in the presence of lead peroxide gives hexachlorodifluorobutene[41].

Krinitsky and Carhart[34] showed that hexachlorobutadiene remains stable for at least 12-15 s at 500°, but at 650° Mamedaliev and coworkers[46] observed the formation of hexachlorobenzene, in an amount which is greatly increased in the presence of carbon tetrachloride, and which is noticeable even at 550°. Although hexachlorobutadiene does not have a flash point, it ignites when sprayed into a stream of gas containing 77% oxygen[47]. The self-ignition temperature of hexachlorobutadiene is 537°.

The passage of chlorine gas through a suspension of various metal oxides in boiling hexachlorobutadiene produces a little phosgene and carbon tetrachloride[48], but unfortunately this paper gives no indication as to whether the reaction vessel was darkened or not, so that the part played by light in this reaction is not known.

Heating equal volumes of hexachlorobutadiene and dilute sodium bicarbonate solution for 4 h at 100° in the presence of iron and with vigorous stirring produced only 0.006 mg of chloride ion per gramme of initial chlorocarbon[8]. This very low degree of hydrolysis may be due to the extremely low solubility of hexachlorobutadiene in water.

Hexachlorobutadiene is stable to strong mineral acids, aqueous alkalis[49], and aqueous solutions of alkali metal hydrogen sulphides at the boiling point[40], the last two clearly also being due to its extremely low solubility in water, since in alcoholic solution hexachlorobutadiene is markedly decomposed by alkali; it has been shown[49] that this first produces 1-ethoxypentachlorobutadiene (I), which

is then converted to 2,4,4,4-tetraethoxy-1,1,3-trichlorobutene (II). An interesting set of reactions has been suggested for this process, in which the addition of alcohol takes place differently at the two ends of the molecule:

$$CCl_2=CCl-CCl=CCl_2 \rightarrow \underset{(I)}{CCl_2=CCl-CCl=CCl\,(OC_2H_5)} \rightarrow$$

$$\rightarrow CCl_2=CCl-CHCl-CCl\,(OC_2H_5)_2 \rightarrow CCl_2=CCl-CCl=C\,(OC_2H_5)_2 \rightarrow$$

$$\rightarrow CCl_2=CCl-CHCl-C\,(OC_2H_5)_3 \rightarrow CHCl_2-CCl\,(OC_2H_5)-CHCl-C\,(OC_2H_5)_3 \rightarrow$$

$$\rightarrow \underset{(II)}{CHCl_2-C\,(OC_2H_5)=CCl-C\,(OC_2H_5)_3}.$$

If sodium ethoxide is used the reaction is more vigorous.

It is interesting to compare these equations with the reaction suggested by Knunyants *et al.*[51] for the corresponding process with hexafluorobuta-1,3-diene:

$$CF_2=CF-CF=CF_2 \rightarrow (C_2H_5O)-CF=CF-CF=CF-(OC_2H_5).$$

The Wurtz reaction proceeds quantitatively with hexachlorobutadiene[52]; this enables the Stepanov method for the analysis of chloro-compounds to be applied to the determination of hexachlorobutadiene.

Dye took out a patent[53] for the production of adducts of hexachlorobutadiene with compounds $P[N(Alk)_2]_3$, where Alk contains 1–4 carbon atoms; these adducts are apparently quaternary ammonium compounds, and can be used as insecticides and rodenticides.

Hexachlorobutadiene does not react with sulphuryl chloride in the presence of benzoyl peroxide[8], nor (unlike butadiene) does it form adducts with dihalogenocarbenes[54].

Fruhwirth reported[5] that hexachlorobutadiene does not react with maleic anhydride or quinone, *i. e.* it does not take part in the Diels–Alder reaction. However, Mamedaliev *et al.* have recently[55] published the results of their diene synthesis with hexachlorobutadiene as the diene component, obtaining hexachlorocyclohexane dicarboxylic acid anhydride in quantitative yield.

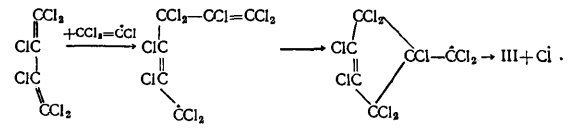
The Diels–Alder reaction of butadiene derivatives having acceptor substituents has been little studied, and in particular the influence of the increased number of chlorine atoms at the double bond of butadiene on the reactivity of polychlorobutadienes is insufficiently known. It is known that maleic anhydride participates in the Diels–Alder reaction with 2-chlorobutadiene, 2,3-dichlorobutadiene[56], and 1,4-dichlorobutadiene[57], but the reaction has not been successful with 2,4-dichlorobutadiene[58], and contacting 1,1,2-trichlorobutadiene with maleic anhydride for 8 h at 180° did not produce the desired results[59]. 1,2,3-Trichlorobutadiene appears to enter into the diene condensation[60].

The increasing difficulty and finally the loss of ability of chlorinated butadienes to act as diene component in the Diels–Alder reaction as the number of chlorine atoms in the molecule is increased may be due to the marked delocalisation of the π electron cloud of the trichlorovinyl group, which causes loss of the $\pi-\pi$ conjugation of the double bonds. The absence of stereoisomeric forms of hexachlorobutadiene does not allow a molecular mechanism to be put forward for the Diels–Alder reaction with this compound as diene component, and the published material[55] requires careful experimental checking. Confirmation of the results obtained would provide the possibility of preparing a large number of new and interesting compounds, many of which would find application as intermediates for the production of polymers, pesticides, and other useful materials.

Hexachlorobutadiene polymerises less readily than hexafluorobuta-1,3-diene[61]. According to Fruhwirth[5] it does not polymerise at pressures up to 100 atm, but above 1870 atm it is partially converted into resinous products[62]. Gonikberg and Zhulin[63] attempted to polymerise hexachlorobutadiene by heating at 350° in a steel bomb for 6 h; the pressure attained is not given, but it apparently reached several hundred atmospheres. In addition to hexachloroethane the reaction products contained a carbon-containing residue, which unfortunately was not further investigated; because the molecular structure of the polymers is not known, the actual starting materials for the polymerisation cannot be established: these could be either hexachlorobutadiene or decomposition products thereof. Alfrey *et al.*[64] were unsuccessful in their attempt to copolymerise hexachlorobutadiene with styrene.

Under the action of an electric discharge[65] hexachlorobutadiene reacts with hydrocarbons (transformer oil) to produce hydrogen chloride, chlorine, low-molecular hydrocarbons, and phosgene.

There is no published material on the action of radiation on hexachlorobutadiene, but Henglein suggests[66] that the radiolysis of tetrachloroethylene produces $CCl_2=\dot{C}Cl$ radicals which combine with one another to form hexachlorobutadiene as an intermediate. According to Miller and coworkers[67] dichloromethylenehexachlorocyclopentene (III) is then produced:



Structure

Batuev and Matveeva[26] consider that the two frequencies which they observed in the double bond frequency region demonstrate interaction between the multiple bonds, *i. e.* conjugation, and they confirm this by consideration of the mean frequency of 1989 cm^{-1}, which is less than the vibrational frequency of the bond in tetrachloroethylene (1571 cm^{-1}).[68] Finally, the high vibrational frequency of the single bond in hexachlorobutadiene (1170 cm^{-1}) by comparison with that of the C–C bond in hexachloroethane (854 cm^{-1})[69] is also related by Batuev and Matveeva to the existence of conjugation. In view of other possible reasons for the appearance of these frequencies, however, the above considerations do not constitute proof of the existence of conjugation between the double bonds.

A discrepancy between the observed molecular refraction and that calculated from the atomic refractions with a correction for the double bonds appears to indicate a certain exaltation, which demonstrates that the molecule has a high polarisability and that the valency electrons are labile.

The non-polar configuration of the hexachlorobutadiene molecule shows that there is insignificant or no overlapping of the π electron clouds, and it can be assumed that the π electrons of the double bonds are to a large extent localised, and conjugation of the double bonds is absent or only minimal.

It would appear that these contradictory results are due to the particular structure of the hexachlorobutadiene molecule, the presence of the six chlorine atoms determining the behaviour of the diene, in view of the strong electric fields created by the electrons of these atoms and the large mass of their nuclei. The interaction between the π electrons of the double bonds is apparently of secondary significance compared with other effects, in particular the interaction of the electrons of the π and σ bonds with the unshared electrons of the chlorine atoms. Some confirmation of this may be found in the slight shift of the ultraviolet absorption spectrum towards longer wavelengths.

Unfortunately, the small amount of existing experimental material throws almost no light on this matter. Roedig[36] has shown that when one molecule of chlorine adds on to hexachlorobutadiene it is the symmetrical isomer which predominates in the reaction products; this may be confirmation of 1,4-addition, but unfortunately no proof was given that octachlorobut-2-ene had in fact been obtained. According to patent data, 1,4-addition accurs in the reaction of hexachlorobutadiene with hydrogen fluoride[39,40], but the products were not identified[40]. The fact that no Diels–Alder adduct has yet been prepared (if the work of Mamedaliev and coworkers[55], which requires careful checking, is discounted) is no proof of the absence of conjugation between the π bonds because of the non-planar configuration of the molecule. The lower stability of the single bond in hexachlorobutadiene in comparison with butadiene is clear from the chlorination of the two compounds. This may be due to the chlorine atoms in hexachlorobutadiene strongly attracting the σ electrons of the symmetrical molecule, so reducing the electron density around the C–C bond. Comparison of the chlorine addition reactions at the double bonds shows that this process is slower in hexachlorobutadiene than in tetrachloroethylene, the explanation of which must also be sought in the particular structure of the hexachlorobutadiene molecule. Further investigation of the physical properties and chemical reactions of hexachlorobutadiene may resolve this matter.

4. BIOLOGICAL PROPERTIES

Hexachlorobutadiene is physiologically active towards plants, insects, and animals.

An aqueous solution of concentration 1-2 mg litre^{-1} suppresses or strongly depresses the growth of the green, blue-green, and diatomic algae[62]: *Microcystis*, *Aphonizomenon*, *Scenedesmus*, *Oosyrtis*, *Navicula*, *Cyclotella*, *Pediastrum*, *Melosira*, *Coelastrum*, and others.

Hexachlorobutadiene is a herbicide for narrow-leaved weeds (grasses) growing among broad-leaved vegetables[70], and is toxic towards a number of insects[70–74] and to grape phylloxera[75]; it has shown high effectiveness against the wintering egg-laying Comstock mealybug *Pseudococcus comstocki*[76], and in concentrations of 0.05–20 mg per kg in water it produces some reaction in certain fish, but without leading to any substantial physiological changes[77].

Of its action on warm-blooded animals and man, the literature only has statements that inhalation of hexachlorobutadiene vapour causes headaches[78] and that its vapour is toxic[79]. It can be assumed that it acts on the living cell principally as a physical poison, *i.e.* it destroys its physicochemical structure, in particular its colloidal state.

5. METHODS OF PREPARATION

The methods for the preparation of hexachlorobutadiene can be divided into three groups: (*i*) those starting from hydrocarbons containing less than four carbon atoms, in which methane or C_2 hydrocarbons are converted into intermediates having four carbon atoms, and these are then converted into hexachlorobutadiene; (*ii*) those starting from C_5 hydrocarbons, involving splitting of the carbon skeleton; and (*iii*) those using normal C_4 compounds as starting material.

A. Preparation of Hexachlorobutadiene from C_1 and C_2 Hydrocarbons

Tolloczko and Kling[80] passed methane with an excess of chlorine at 400° through a tube containing pumice, and found a little hexachlorobutadiene in the reaction products.

As early as 1893 Besson reported[1] on the thermal conversion of chloroform into hexachlorobutadiene, and it has recently been shown[81] that despite Besson's inaccurate description of the compound, hexachlorobutadiene is in fact produced from chloroform. In a continuous process the yield of hexachlorobutadiene from chloroform is 15.6% at 550°. Decreasing the time of reaction at a higher temperature or increasing the residence time of the reactants in the reaction zone at a lower temperature reduce the yield of hexachlorobutadiene.

Most papers relate to the preparation of hexachlorobutadiene from compounds obtained from acetylene. Fruhwirth[84] proposed the production of hexachlorobutadiene from acetylene and chlorine in a single stage at 600–950°; the yield of desired product was 40%. It may be assumed that this process passes through diacetylene, hexachlorobutene, and octachlorobutane by the reactions set out below[83]. This is the shortest route for obtaining hexachlorobutadiene from a hydrocarbon, but is difficult to carry out because of the need for removing a large amount of heat and because of the recirculation of a considerable quantity of the hexachlorobutadiene. A process which follows the above mechanism has been proposed[82], starting from diacetylene[93], which is chlorinated at -30° to -25° to obtain a mixture of isomers of 1,1,2,3,4,4-hexachlorobut-2-ene in 73–80% yield; this mixture is then treated with liquid chlorine under pressure with prolonged irradiation with a quartz lamp to obtain 1,1,2,2,3,3,4,4-octachlorobutane in 76–91% yield, which on dehydrochlorination with aqueous alcoholic sodium hydroxide solution[84] produces hexachlorobutadiene in 67% yield. Since diacetylene is the main by-product in the production of acetylene from hydrocarbons, this method may be of practical interest.

Octachlorobutane can also be dehydrochlorinated by Roedig's method[85] using various metals in ether solution in the presence of aluminium chloride, or by heating at 190–200° in the presence of iron(III) chloride[84].

Keller and Keyssner[86] have proposed the production of hexachlorobutadiene from monovinylacetylene in two stages, by way of 1,2,3,3,4,4-hexachlorobutane.

The preparation of hexachlorobutadiene from butynediol has also been suggested[87]. Butynediol is reacted with thionyl chloride by Johnson's procedure[88], the resulting 1,4-dichlorobutyne is chlorinated at a temperature of -40° to -50° to give 1,2,2,3,3,4-hexachlorobutane in ~98% yield,

and this is then dehydrochlorinated with KOH in 50% yield. The 1,2,3,4-tetrachlorobutadiene is chlorinated in the presence of antimony trichloride at 30–50° to produce hexachlorobutene, which is reacted with chlorine under pressure in sealed ampoules with ultraviolet readiation to give octachlorobutane in 91% yield; this is dehydrochlorinated to hexachlorobutadiene [83].

An Austrian patent [89] describes the production of hexachlorobutadiene from chlorinated derivatives of ethane or ethylene. As gaseous mixture of 3 volumes of trichloroethane and 2 volumes of chlorine is passed rapidly through a porcelain tube at 500°, when the chlorination product contains 30% hexachlorobutadiene. Catalysts may be used. The same patent claims that polychloroethanes or polychloroethylenes can be chlorinated in a reactor as used for the production of hydrogen chloride from its elements or in an apparatus used for the high-temperature chlorination of acetylene. The reaction products contain 20% hexachlorobutadiene, corresponding to a yield of 40% based on tetrachloroethylene.

The production of hexachlorobutadiene from trichloroethylene has been described [90]. When trichloroethylene and chlorine were passed over active carbon at 350–400° the reaction product contained over 50% hexachlorobutadiene. In another case, trichloroethylene first gave 1,1,1,2,3,4-hexachlorobut-3-ene, which was passed through the catalyst at 280–300°; the yield of hexachlorobutadiene was 85%. The catalyst was activated carbon impregnated with barium chloride. The use of copper or iron chlorides or their mixtures, which may be deposited on various carriers, is also recommended.

Hexachlorobutadiene is obtained in a small amount in the continuous production of trichloroethylene by the dehydrochlorination of tetrachloroethane at 520°. [91] Wimmer [92] has shown that 1,1,2,3,4,4-hexachlorobutane and 1,2,3,4,-tetrachlorobutadiene, which are obtained in the industrial production of tri- and tetra-chloroethylene, can also be converted into hexachlorobutadiene by treating the corresponding fraction with chlorine at 70–80° in the presence of 0.1% iron(III) chloride, when 1,1,2,3,4,4-hexachlorobutane produces 1,1,1,2,3,4,4,4-octachlorobutane and 1,2,3,4-tetrachlorobutadiene produces 1,1,2,2,3,3,4,4-octachlorobutane; the resulting mixture is then heated at 100–140° to obtain hexachlorobutadiene in 90% yield. The production of hexachlorobutadiene from hexachlorobutene is similar [93].

Gonikberg and Zhulin [62,63,94,95] have also obtained hexachlorobutadiene from tri- and tetra-chloroethylene. The main product from trichloroethylene at 200–250° and pressures up to 1300 atm is 1,1,2,4,4-pentachlorobuta-1,3-diene (produced by dehydrochlorination of the trichloroethylene dimer 1,1,3,3,4,4-hexachlorobutene which is first formed); chlorination followed by dehydrochlorination then gives hexachlorobutadiene. The chlorination has been effected by Roedig's procedure [96], at 200° with irradiation by a 500 W bulb; subsequent distillation of the reaction products gave heptachlorobutene and hexachloroethane in yields of 32 and 12 wt.% respectively, and it is interesting that hexachlorobutadiene was also obtained, in 35% yield. The formation of a considerable amount of hexachlorobutadiene may be due both to dehydrochlorination of the heptachlorobutene, and to substitutive chlorination of the initial pentachlorobutadiene. The action of alcoholic alkali using Roedig's method [96] on the comparatively wide heptachlorobutene fraction gave hexachlorobutadiene in 75% yield.

Heating tetrachloroethylene at 350° and pressures up to 1870 atm produces hexachlorobutadiene and hexachloroethane [63], the amount of the former decreasing as the pressure is increased because of the accelerating effect of pressure on the thermal conversion of hexachlorobutadiene into resinous products. The formation of hexachlorobutadiene is thought to be a chain reaction:

$$2C_2Cl_4 \rightarrow \dot{C}_2Cl_3 + \dot{C}_2Cl_5,$$

$$\dot{C}_2Cl_3 + C_2Cl_4 \rightarrow CCl_2{=}CCl{-}CCl_2{-}\dot{C}Cl_2,$$

$$CCl_2{=}CCl{-}CCl_2{-}\dot{C}Cl_2 + C_2Cl_4 \rightarrow CCl_2{=}CCl{-}CCl{=}CCl_2 + \dot{C}_2Cl_5,$$

$$\dot{C}_2Cl_5 + C_2Cl_4 \rightarrow C_4Cl_6 + \dot{C}_2Cl_3,$$

with termination by the reaction:

$$2\dot{C}_2Cl_3 \rightarrow C_4Cl_6.$$

A defect of both methods of obtained hexachlorobutadiene is the use of high pressure, and also the fact that they are multistage processes, since the production of tri- or tetra-chloroethylene from hydrocarbons is itself an independent process.

Trichloroethylene can also be dimerised without the use of pressure. Frank and Blackham [97] used azodiisobutyronitrile (Porofor N) and obtained 1,1,3,3,4,4-hexachlorobut-1-ene in 61.5% yield; the same product is obtained with benzoyl peroxide [98]. Boiling trichloroethylene in the presence of aluminium chloride causes dimerisation and dehydrochlorination with the formation of 1,1,2,4,4-pentachlorobutadiene in 12% yield [99]. The conversion of these two compounds into hexachlorobutadiene can also be effected without pressure [100], but the described methods for obtaining hexachlorobutadiene from trichloroethylene suffer from being multistage processes.

The production of hexachlorobutadiene in 75% yield by chlorinating 1,3-dichlorobut-2-ene at 475° has been described [7,101,102], and might be of practical interest where dichlorobutene, a by-product in chloroprene manufacture, is readily available, but a special synthesis of dichlorobutene from acetylene would make this method cumbersome.

Fig. 2 shows the methods for the production of hexachlorobutadiene from acetylene. With methods starting from methane or chlorinated methanes the yield of hexachlorobutadiene is low; starting from acetylene a multistage process is necessary.

B. Production of Hexachlorobutadiene from C_5 Hydrocarbons

In most of these methods the hexachlorobutadiene is formed as a by-product in 10–25% yields in the production of hexachlorocyclopentadiene from polychloropentanes, the carbon chain being broken [103-105].

A higher yield, up to 60%, is attained in the chlorinolysis of octachloropenta-1,3-diene [11]. Since the formation of hexachlorocyclopentadiene from pentane or polychloropentanes proceeds by way of octachloropenta-1,3-diene and octachlorocyclopentene [106], the formation of hexachlorobutadiene in the process is apparently due to decomposition of the intermediately formed octachloropenta-1,3-diene. The yield of octachloropenta-1,3-diene in the chlorination of polychloropentanes has been raised to 30% by recycling

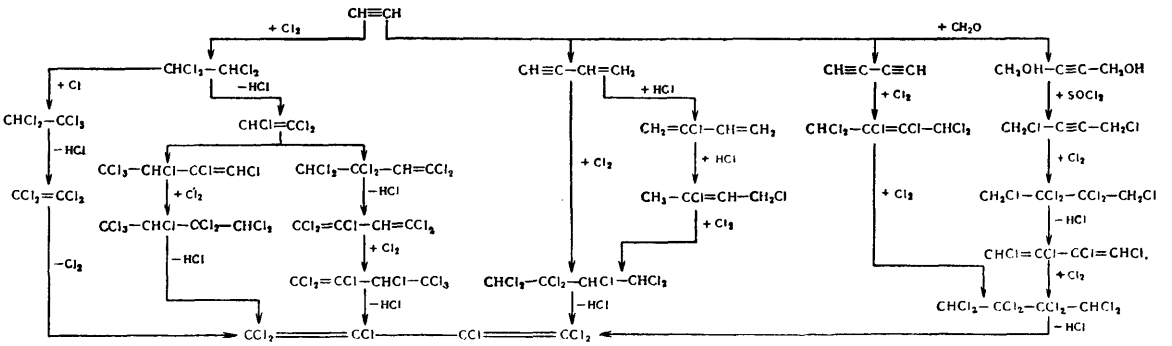


Fig.2. Reaction schemes for the conversion of acetylene into hexachlorobutadiene.

the octachlorocyclopentene[107]; the overall yield of hexachlorobutadiene from pentane or polychloropentanes is thus 15–20%.

These methods for the production of hexachlorobutadiene are of secondary importance, since the main product of the extensive chlorination of C_5 hydrocarbons is hexachlorocyclopentadiene.

C. Production of Hexachlorobutadiene from C_4 Hydrocarbons

This group of methods has the most pratical interest, since it provides the shortest route from hydrocarbon to product. The starting material may be n-butane, the isomeric straight-chain butylenes, or butadiene; isobutane and isobutylene are unsuitable, since under the conditions studied these or their polychloro-derivatives do not isomerise to straight-chain compounds, but are decomposed.

The methods for obtaining hexachlorobutadiene from C_4 hydrocarbons can be divided into two groups[108]. One includes two-stage processes involving the production of polychlorobutanes which are then converted into the desired product, and the other embraces single-stage conversions of the hydrocarbons into hexachlorobutadiene.

Nearly all published work on the chlorination of butane has related to the production of monochlorides, so that polychlorides are obtained in small amounts and are generally dichlorides containing only small amounts of trichlorobutanes. Light[8] and chemical initiation[109-111] have generally been employed for chlorinating butane or its polychloro-derivatives to obtain polychlorobutanes having a considerable chlorine content.

In their article on the production of hexachlorobutadiene, McBee and Hatton[8] report the use as starting materials of the polychlorobutanes obtained by chlorinating butane at 80–90° in the presence of light; the butane was completely converted into a mixture of chlorobutanes, of average composition $C_4H_4Cl_6$. A mixture of polychlorobutanes of about the same composition was also obtained by another method.

Another procedure[109] used as starting material the mixture of trichlorobutanes obtained in small amount in the thermal chlorination of butane; this was subjected to liquid-phase chlorination in the dark, with Porofor as initiator.

Kogan and Ignatova have made a detailed investigation of the chlorination of butane[110,111], using carbon tetrachloride, hexachlorobutadiene, and the chlorination products as reaction medium and Porofor as initiator. They studied the influence of the reaction conditions on the extent of the reaction between butane and chlorine and on the extent of the chlorination.

In addition to chemically irreversible reactions, physical equilibrium processes (dissolution of gases), which determine the mass transfer, also play a significant part, and their influence on all processes must be taken into account when considering the results of any study. Thus increase of temperature should increase the rate of dissolution of gases, their diffusion in the liquid, and the rate of chlorination reactions, but at the same time the solubility of butane and chlorine in the liquid will decrease. Increasing the molar ratio of chlorine to butane creates favourable conditions for the dissolution of butane, because of its decreased partial pressure in the gas mixture. Different conditions will arise in the solution in respect of the chlorination of butane and polychlorobutanes, because of the low concentration of butane in the reaction mixture in comparison with the polychlorobutane content. The difference in these concentrations is apparently not compensated by the presence in the butane molecule of the more reactive hydrogen atoms of the methylene groups, these being absent or present to a lesser extent in the polychlorobutanes.

The formation of two molecules from two radicals thermodynamically provides the possibility of the reverse reaction, the production of two radicals from two valency-saturated molecules[112].

The energy of activation of the reaction

$$CH_3{=}CH_3{+}Cl_2 \rightarrow CH_3Cl{-}CH_3{+}Cl$$

is 41 kcal, *i.e.* considerably less than 57 kcal which is the energy of activation for the dissociation of chlorine molecules into atoms. The transition to butylene and butadiene leads to a decrease in the energy of activation for the formation of the corresponding radical. This opens up the possibility of using this method of initiating the

reaction of butane with chlorine not only for the preparation of monochlorobutane[113], but also for the production of more highly chlorinated products. This was the basis of experiments[111,114] in which butane was highly chlorinated in the presence of butylene and butadiene instead of the known initiators. The addition of 15–20% of butylene to the butane under the reaction conditions previously used[110] produces tetrachlorobutanes, and if butadiene is used instead of butylene, pentachlorobutanes are obtained. When butylene or butadiene is chlorinated, the addition of chlorine to the double bonds is accompanied by substitutive chlorination[115].

The production of polychlorobutanes in these reactions can be represented as follows:

from butylene

$$CH_3-CH=CH-CH_3 \xrightarrow{+Cl_2} CH_3-CHCl-\dot{C}H-CH_3+\dot{C}l \rightarrow CH_3CHClCHCl-CH_3 \xrightarrow[-HCl]{+Cl^\cdot} \longrightarrow \dot{C}_4H_7Cl_3 \xrightarrow{+Cl_2} C_4H_7Cl_3+Cl^\cdot \xrightarrow[-HCl]{} \dot{C}_4H_6Cl_3 \xrightarrow{+Cl_2} C_4H_6Cl_4+\dot{C}l \text{ etc.},$$

and from butadiene

$$CH_2=CH-CH=CH_2 \xrightarrow{+Cl_2} CH_2Cl-CH=CH-\dot{C}H_2+Cl^\cdot \rightarrow$$
$$\rightarrow CH_2Cl-CH=CH-CH_2Cl \xrightarrow{+Cl_2} CH_2Cl-CHCl-\dot{C}H-CH_2Cl+\dot{C}l \rightarrow$$
$$\rightarrow CH_2Cl-CHCl-CHCl-CH_2Cl \xrightarrow[-HCl]{+Cl_2} \dot{C}_4H_5Cl_4 \xrightarrow{+Cl_2} C_4H_5Cl_5+\dot{C}l \text{ etc.}$$

The use of these unsaturated compounds instead of Porofor, benzoyl peroxide, or other such initiators avoids the use of expensive and explosive substances and simplifies the production of polychlorobutanes.

When butane is chlorinated the hydrogen atoms on the secondary carbon atoms are first replaced, because of the smaller energy required in forming the corresponding free radical. The tendency after this is to produce symmetrical molecules, so that if the final products are hexachlorobutanes the predominant isomer will be 1,2,2,3,3,4-hexachlorobutane.

The chlorination of polychlorobutanes to produce hexachlorobutadiene, which takes place in the gas phase either without[8,35,116,117] or with a catalyst[34,109,118], has already been reviewed[9], and we shall consider here only work published since 1959.

The production of hexachlorobutadiene from trichlorobutanes over diatomite[109] has been confirmed by Nekrasova and Shuikin[119], who used as catalyst specially treated Crimean coquina and a mixture of chromium, aluminium, and magnesium oxides, and obtained hexachlorobutadiene in yields of 57 and 37% respectively. Dilution of the chlorine with an equal volume of nitrogen increased the yield to 66–68%, but it did not reach 76% as in the previous method[109].

Kogan and Burmakin[35] made thermodynamic calculations and carried out a comparative investigation of the chlorination of polychlorobutanes in the absence of a catalyst and in the presence of diatomite, using the following reactions:

$$CH_2Cl-CCl_2-CCl_2-CH_2Cl+Cl_2 \rightarrow CHCl_2-CCl_2-CCl_2-CH_2Cl+HCl, \quad (a)$$
$$CHCl_2-CCl_2-CCl_2-CH_2Cl+Cl_2 \rightarrow CHCl_2-CCl_2-CCl_2-CHCl_2+HCl, \quad (b)$$
$$CHCl_2-CCl_2-CCl_2-CHCl_2 \rightarrow CCl_2=CCl-CCl_2-CHCl+HCl, \quad (c)$$
$$CCl_2=CCl-CCl_2-CHCl_2 \rightarrow CCl_2=CCl-CCl-CCl_2+HCl, \quad (d)$$

Fig. 3 shows the results of the thermodynamic calculations.

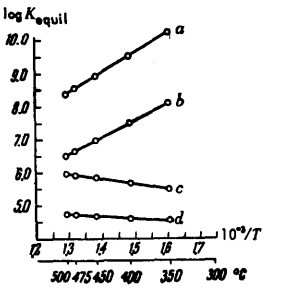


Fig. 3. Variation of the equilibrium constant with the reaction temperature in the chlorination of hexachlorobutane to hexachlorobutadiene.

All the reactions are irreversible over a wide temperature range; reaction (d) is the limiting stage. The equilibrium constant for reaction (c) decreases with the temperature considerably more rapidly than the equilibrium constant for reaction (d).

One of the interesting questions which arise in the study of hexachlorobutadiene production is the influence of the chlorine content of polychlorobutanes when they are reacted with chlorine at elevated temperatures (Fig. 4). Figs. 5, 6, and 7 show the influence of other factors on the process.

Polychlorobutanes react with chlorine to produce hexachlorobutadiene, decomposition products, and resins. The decomposition products apparently arise because of cracking of the higher polychlorobutanes. Lower polychlorobutanes mainly undergo further chlorination, while hexachlorobutadiene is stable under the reaction conditions in

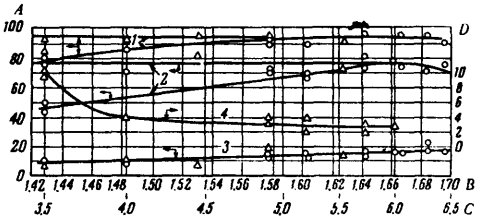


Fig. 4. Influence of the degree of chlorination of butane on the reaction of polychlorobutanes with chlorine. In the absence of catalyst: excess of chlorine 40–50%, t_1 = 350°, l_1 = 120 mm, t_2 = 475°, l_2 = 750 mm, rate of feed of polychlorobutanes (PCB) 0.35–0.40 g-mole h^{-1}. Over diatomite: excess of chlorine 40–50%, t_1 = 350°, l_1 = 120 mm, t_2 = 425°, l_2 = 750 mm, rate of feed of PCB 0.33–0.35 g-mole h^{-1}. *A* is yield in %, *B* is the specific gravity of the PCB, *C* is the number of chlorine atoms in the PCB molecule, and *D* is the amount of involatile residue in wt.%; 1) conversion of the PCB; 2) yield of C_4Cl_6; 3) yield of decomposition products; 4) amount of involatile residue. Circles represent absence of catalyst, triangles represent use of diatomite.

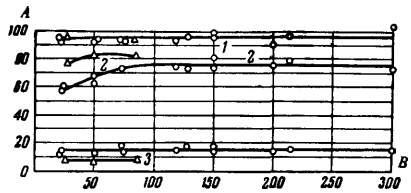


Fig.5. Influence of the excess of chlorine on the gas-phase chlorination of polychlorobutanes. In the absence of catalyst: PCB $d_{20}^{20} = 1.6423$, $n_D^{20} = 1.5290$, rate of feed 1.6–1.7 g min^{-1}, $t_1 = 350°$, $l_1 = 120$ mm, $t_2 = 475°$, $l_2 = 750$ mm. Over diatomite: PCB $d_{20}^{20} = 1.4344$, $n_D^{20} = 1.5010$, rate of feed 0.5 g min^{-1}, $t_1 = 350°$, $l_1 = 120$ mm, $t_2 = 450°$, $l_2 = 750$ mm. *A* is yield, %, *B* is excess of chlorine, %; 1) conversion of the PCB; 2) yield of C_4Cl_6; 3) yield of decomposition products. Circles and triangles as in Fig.4.

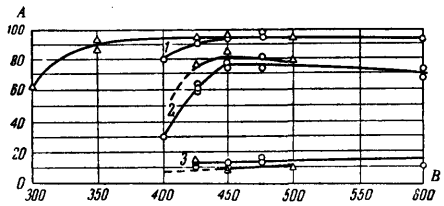


Fig.6. Influence of temperature on the chlorination of polychlorobutanes. In the absence of catalyst: $d_{20}^{20} = 1.6423$, $n_D^{20} = 1.5290$, excess of chlorine 150%, $t = 350°$, $l_1 = 120$ mm, $l_2 = 750$ mm, rate of feed of PCB 1.6–1.7 g min^{-1}. Over diatomite: excess of chlorine 45–55%, $t_1 = 350°$, $l_1 = 120$ mm, $l_2 = 750$ mm, rate of feed of PCB ($d_{20}^{20} = 1.4344$, $n_D^{20} = 1.5010$) 0.5 g min^{-1}. *A* is the yield, %, *B* is the temperature, °C; 1) conversion of PCB; 2) yield of hexachlorobutadiene; 3) yield of decomposition products. Circles and triangles as in Fig.4.

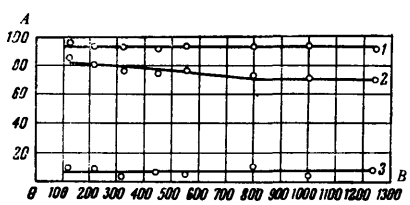


Fig.7. Influence of loading rate of the polychlorobutanes on their overall conversion and on the yield of hexachlorobutadiene and decomposition products over diatomite. PCB $d_{20}^{20} = 1.4344$, $n_D^{20} = 1.5010$, $t_1 = 350°$, excess of chlorine 45–55%, $l_1 = 120$ mm, $t_2 = 450°$, $l_2 = 750$ mm. *A* is the yield, %; *B* is the loading rate of the PCB, kg m^{-3} h^{-1}; 1) conversion of the PCB; 2) yield of C_4Cl_6; 3) yield of decomposition products.

the absence of a catalyst. The greater degree of chlorination of polychlorobutanes of the same chlorine content when the reaction is effected over diatomite, as compared with reaction in the absence of a catalyst, demonstrates the increased rate of the process in the former case, *i.e.* the catalytic action of the diatomite; this is also seen in the lower temperature required when diatomite is used. The presence of diatomite (or other porous material) in the reaction zone has a number of technological advantages. Packing the reactor favours mixing, and the retention of the chlorine in the pores of the contact mass enables the amount of chlorine feed to be reduced.

Hexachlorobutadiene can be produced from C_4 hydrocarbons in a single step in the absence [120] or presence of a catalyst [92,120], including a fluidised-bed catalyst [105,121,122], or in an orifice burner [104]. The single-stage methods require the use of a large excess of chlorine, which raises the difficulty of extracting chlorine from the exit gases and recycling it; this can be met by using hexachlorobutadiene (see below).

6. SOME MATTERS CONCERNING THE INDUSTRIAL PREPARATION

A number of problems arise in the production of hexachlorobutadiene on a commercial scale; we shall consider only three: the choice of material for the high-temperature chlorination reactor, the separation of the reaction products, and the purification of the hexchlorobutadiene.

For chlorination under industrial conditions, only nickel is suitable for the reactor, if porcelain [120], which is not suitable for construction purposes, and graphite [120], which is not very convenient and will apparently react with the chlorine, are not taken into account. Carbon steel, various iron alloys, including EZh-17† and EYa1T‡, cast iron, and many metals (aluminium, copper, lead, magnesium, silver, gold, and platinum) are unsuitable because of their corrosion [123,124]; moreover certain metal chlorides, *e.g.* of iron, cause polymerisation of the unsaturated intermediates and so produce resinification.

The rate of corrosion of nickel by chlorine at 500° is 0.5 g m^{-2} h^{-1}; raising the temperature by only 40° increases the rate of corrosion to 2.1 g m^{-2} h^{-1}, and the use of a maximum temperature of ~500° is therefore recommended [123,124]. It is important to note that with prolonged working of the reactor the actual temperature must apparently be lower, because of the gradual evaporation of the protective film of nickel chloride and the formation of a new film, *i.e.* corrosion of the nickel. A large excess of chlorine aids the evaporation of the nickel chloride.

When chlorination has been properly carried out, the liquid reaction products have considerably different boiling points and can be readily separated. With incomplete chlorination of the starting materials, the reaction product will contain, in addition to chlorocarbons, highly chlorinated polychlorobutanes, polychlorobutenes, and polychlorobutadienes, and these impurities are very difficult to remove because they have boiling points close to

† Cr 16.0–18.0, Ni ≯ 0.60, C ≯ 0.12, Si ≯ 0.80, Mn ≯ 0.70, S ≯ 0.030, P ≯ 0.035% (Ed. of Translation).

‡ Cr 17.0–20.0, Ni 8.0–11.0, C ≯ 0.12, Si ≯ 0.80, Mn ≯ 2.0, S ≯ 0.030, P ≯ 0.035%, stabilised with Ti from (C–0.03)× 5 to 0.08% (Ed. of Translation).

that of hexachlorobutadiene. The presence of these impurities in commercial hexachlorobutadiene renders the latter unstable on storage and in certain of its uses; in particular the physical properties of the liquid (especially its electrical properties) deteriorate and it gives off hydrogen chloride, etc. Chemical methods have been suggested for purifying the hexachlorobutadiene; one[50] is based on its stability towards aqueous solutions of alkali metal hydrogen sulphides, the chlorine atoms in polychlorobutanes being replaced by the thiol group; according to another[125] the impure hexachlorobutadiene is treated with non-alkaline substances which can take up hydrogen chloride: carbohydrates (*e.g.* sucrose), sawdust, paper, or cotton.

Sometimes the reaction products contain a considerable quantity of hexachloroethane (b.p. 187°); to prevent this crystallising on the walls of the condenser, injection of water has been suggested[92], which prevents adhesion of the hexachloroethane particles to the walls, or the addition to the initial mixture of a substance whose boiling point is near that of hexachloroethane.

7. FIELDS OF USE

The uses of hexachlorobutadiene are based on its comparative chemical stability, especially its non-inflammability, and its particular combination of physical properties. It has been proposed for use in hydraulic[126-131] and electrically insulating[11,33,118,126,127,131] liquids, as a lubricant[126] and solvent[118], and, to a lesser extent, as a chemical reagent and pesticide.

One of the most interesting uses of hexachlorobutadiene is as a dispersion medium in the determination of the infrared spectra of various substances[132,133]. The paraffin oil used for this purpose has strong absorption bands at 3.4, 6.85, and 7.26 μm and weaker bands at 2.4, 3.8, and 13.8 μm, which considerably limit its range of applicability. Hexachlorobutadiene can be used over practically the whole range of infrared spectra, except for the regions of frequency 1640–1510, 1200–1140, and 1010–760 cm^{-1}, where the absorption exceeds 25%.[134] Hexachlorobutadiene is widely used in spectroscopy[135-142].

An important problem in the production of chlorinated organic compounds is the purification of the hydrogen chloride given off in the chlorination from unreacted chlorine and volatile organic compounds. Until recently this had been achieved by absorbing the hydrogen chloride in hydrochloric acid followed by desorption, but this method has many disadvantages. In 1958 a patent was taken out[143,144] for obtaining pure hydrogen chloride by washing the chlorination gases first with carbon tetrachloride and then with hexachlorobutadiene (Fig. 8). The first wash dissolves chlorine and the organic compounds, which are separated by rectification and recycled to the chlorination; the second wash dissolves the volatile CCl_4 entrained by the hydrogen chloride in the first wash. Both washing columns are operated at 35°. After a further wash with hexachlorobutadiene under pressure at -15° the hydrogen chloride is almost free of carbon tetrachloride and contains less than 0.01% by weight of hexachlorobutadiene and less than 0.001% of chlorine. The initial cost using this method is half that using the hydrochloric acid method[145], and it is in use in the USA.[146]

Hexachlorobutadiene has been used as a solvent for chemical reactions; of most interest is its use as a chlorination medium, and indeed it is difficult to find another compound

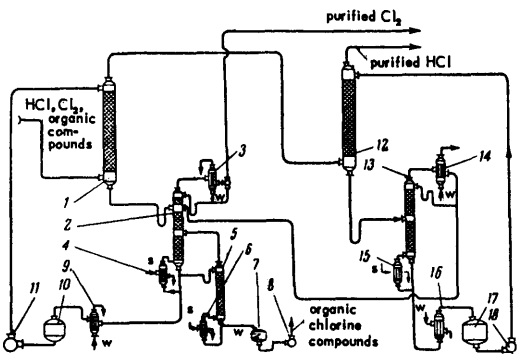


Fig. 8. Principle scheme for the purification of hydrogen chloride with carbon tetrachloride and hexachlorobutadiene:
1) absorber for Cl_2 and organic compounds; 2) chlorine desorber; 3) dephlegmator; 4) boiler; 5) column for the separation of the organic compounds; 6) boiler; 7) receiver for organic compounds; 8) pump for organic compounds; 9) CCl_4 condenser; 10) CCl_4 receiver; 11) pump for CCl_4; 12) CCl_4 absorber; 13) column for separating CCl_4; 14) dephlegmator; 15) boiler; 16) C_4Cl_6 condenser; 17) C_4Cl_6 receiver; 18) pump for C_4Cl_6; w = water, s = steam.

which is so inert towards chlorine up to 215°. A patent[147] recommends the chlorination of paraffin and rubber in hexachlorobutadiene.

A recent paper[48] describes the selective chlorination of metal oxides in boiling hexachlorobutadiene to separate metals of similar properties. A metal chloride is produced quantitatively and dissolves in the boiling chlorocarbon, separating out when the solution is cooled to room temperature; $MoCl_4$, $NbCl_5$, and $FeCl_3$ can be obtained in this way from the corresponding oxides. Other oxides, in particular MoO_3, Cr_2O_3, and Ta_2O_5, react little or not at all under these conditions.

Hexachlorobutadiene is recommended as a solvent for obtaining hexachlorocyclopentadiene dimer[148,149], and also for the investigation of the mechanism[150] and kinetics[151] of reactions.

Hexachlorobutadiene has been used as an additive for high-pressure lubricating oils[152]. It can be added to motor fuel with tetraethyl lead, which has the same vapour pressure as hexachlorobutadiene[153]; the addition of the latter apparently acts to remove the lead from the engine as lead chloride. Studies of the vulcanisation of RGS rubber with hexachlorobutadiene[154] have shown it to be inactive or only weakly active in the reaction.

An extremely important use of hexachlorobutadiene is as a biologically active material. It has been suggested[155-157] that the physical and chemical properties of some highly effective pesticides, which determine the duration of their retention at the site of the biological objective, are of greater significance than their toxicity. This may happen when the living organisms inhabit media (water, soil) which are comparatively active towards the chemicals added; thus in selecting pesticides for organisms in such media the aim should be to find compounds which are

stable over a period of time. These considerations have led to the investigation of hexachlorobutadiene for use against lower aquatic plants and certain soil pests.

Hexachlorobutadiene has been proposed for the suppression of the growth of algae in fresh water[69,158].

The addition of small doses of hexachlorobutadiene to vineyard soil successfully combats the most serious grape disease, phylloxera[75,159]. This work led to considerable investigation of the proposed use of a fumigant for this purpose[76,160-171]. The particular features of hexachlorobutadiene in comparison with known phylloxerocides (carbon disulphide, dichloroethane, and other polychloroethanes and propanes) are the manifestation of activity only 3–4 months after its introduction into the soil, its penetration throughout the whole depth of the root system, its lasting action (at least 3–4 years), and its application in smaller doses. Hexachlorobutadiene is added to the soil in amounts of 15 to 25 g m^{-2}, depending on the local conditions. At such doses there is practically complete mortality of the phylloxera, with no effect on the biochemical indices of the fruit (sugar content, acidity), and, in some cases, stimulation of growth of the plant. Larger doses have an adverse effect on the plant. A procedure is being developed for using hexachlorobutadiene in separate soil climatic zones in viniculture. Thus the reflections given above on the choice of pesticides have led to the use of hexachlorobutadiene, which is not outstandingly toxic among chlorine compounds, as a highly effective pesticide against certain organisms in media where such other compounds would be considerably less effective.

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ADVANCES IN THE CHEMISTRY OF THIAMINE

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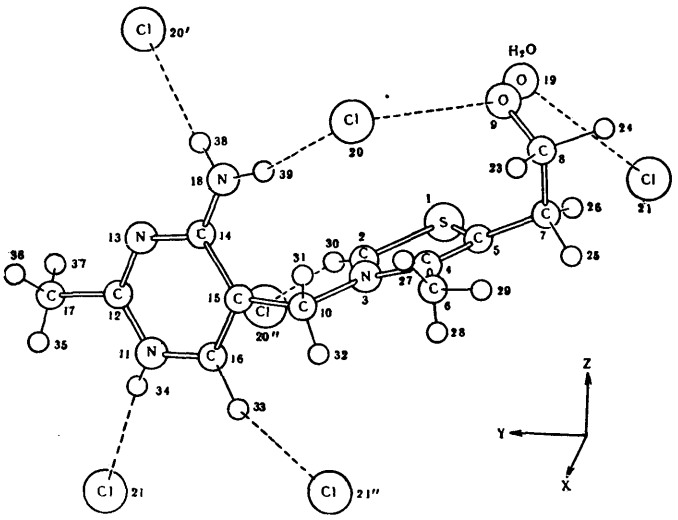


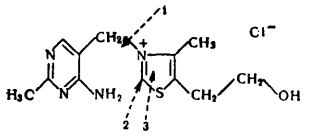
Three-dimensional model of vitamin B_1.

I. INTRODUCTION

The main lines of research and the results obtained during recent years on one of the most important vitamins of the B group, thiamine, have consisted in the development and improvement of manufacturing processes, a more thorough investigation of chemical properties, and finally elucidation of the mechanism of its action in biochemical processes.

Thiamine, whose structure was established in 1936, is now produced annually in tens and hundreds of tons in many countries of the world. The methods for its production are continually being improved. Tens of derivatives of thiamine are known which possess varying biological activity and have varied clinical applications. The synthesis of analogues of thiamine and the investigation of their properties have acquired great significance, their study having promoted an understanding of the role of individual structural groupings in the vitamin molecule. Finally, the detailed investigation of the chemical properties of thiamine has enabled new products to be synthesised (propyl thiamine disulphide, *S*-benzoylthiamine *O*-monophosphate, etc.) and the mechanism of the biochemical action of vitamin B_1 to be elucidated.

The chemical properties of thiamine and its derivatives are determined to a large extent by the extremely reactive thiazolium ring.



The known reactions of thiamine can be divided into two groups: (i) reactions (1) and (2) which do not involve cleavage of the thiazolium ring; and (ii) reactions (3) which result in cleavage of the thiazole ring with formation of various derivatives of the unsaturated thiol. The arrows with attached numerals in the above formula show the direction of attack of reagents in the various processes.

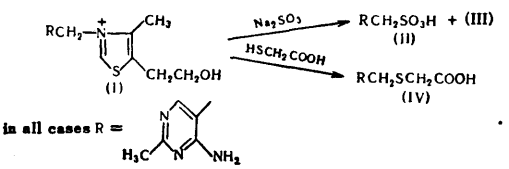
A recent X-ray analysis of thiamine chloride has established interesting peculiarities in the spatial structure of the vitamin. The accompanying diagram shows a projection of a three-dimensional model. The planes of the pyrimidine and thiazolium rings are at an angle of 76° to one another. As a result of this relative arrangement of the rings, position 2 in the thiazole ring is not shielded by the amino-group.

II. REACTIONS NOT INVOLVING CLEAVAGE OF THE THIAZOLIUM RING

1. Sulphite Cleavage of Thiamine

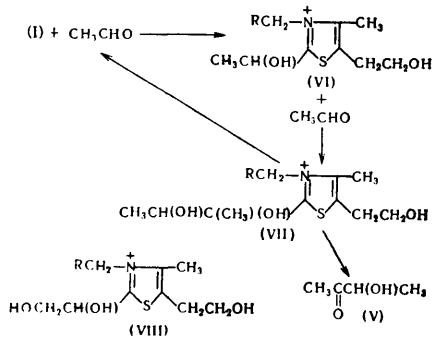
Sulphite cleavage of thiamine (I) leads to the formation of 4-amino-2-methylpyrimidin-5-ylmethanesulphonic acid (II) and 2-(4-methylthiazol-5-yl)ethanol (III). A recent reinvestigation of this reaction[2] has shown it to be specific to thiamine derivatives containing a quaternary nitrogen atom. Thus cleavage of the vitamin is not observed in strongly alkaline solutions, in which thiamine exists in the thiol form. In concentrated solution hydrogenated derivatives of thiamine (containing a tertiary nitrogen atom in the thiazoline ring) also are not cleaved. In dilute solutions they are oxidised to thiamine, after which the usual cleavage of the vitamin takes place.

Reaction with thioglycollic acid also results in the degradation of thiamine, with the formation of a pyrimidinylmethyl sulphide (IV) and the substituted thiazole (III):[3]



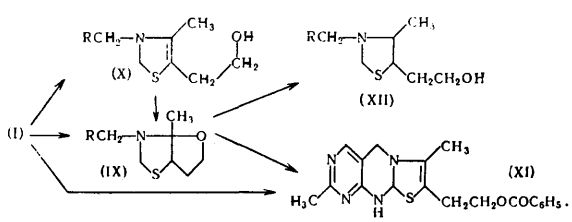
2. Reactions of Thiamine with Carbonyl Compounds

The interaction of thiamine with carbonyl compounds represents a typical electrophilic substitution. Investigation of this reaction has established the role of thiazolium derivatives as natural catalysts for aldol condensations. Mizuhara[4] was the first to observe that acetoin (V) is formed when thiamine is treated with pyruvic acid in weakly alkaline medium (pH 8.5). Condensation of thiamine with acetaldehyde under these conditions results in "α-hydroxyethylthiamine" (VI), in which the hydroxyethyl group has been added at position 2 of the thiazole ring. Another compound is also formed, and is found to have the structure of an "acetointhiamine" (VII).[5] Thus the formation of acetoin from acetaldehyde in non-enzymatic processes involves the following reactions:



The reaction is general in character[5], formaldehyde under these conditions giving a dihydroxyethyl derivative of thiamine (VIII). The analogous reactions with hydroxyacetaldehyde and hydroxypyruvic acid result in the formation of mixtures of sugars.

3. Hydrogenation of Thiamine

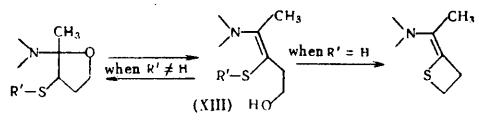


Investigation of the properties of dihydrothiamine, which is formed by the hydrogenation of thiamine[10], has shown that in fact it has the structure of a perhydrofurothiazole[6] (IX), as has been confirmed by comparing the infrared spectra of dihydrothiamine with those of substances possessing an analogous structure. Only very cautious reduction of thiamine with sodium hydrotrimethoxyborate gave the isomeric dihydrothiamine (X), in which closure of the hydrogenated furan ring could be effected simply by heating in water[7]. In addition to these substances, hydrogenation also yields a pseudodihydrothiamine, which has been found to be a pyrimido[4,5-*d*]thiazolo[3,4-*a*]pyrimidine[8]. Benzoylation of dihydrothiamine in pyridine yields the benzoate of the pseudo-form (XI).[11] Reduction of thiamine and of dihydrothiamine with sodium tetrahydroborate gives tetrahydrothiamine (XII).[9]

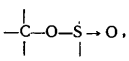
III. REACTIONS RESULTING IN CLEAVAGE OF THE THIAZOLIUM RING

1. Inactive Thiamine; Formation of Thiamine Anhydride

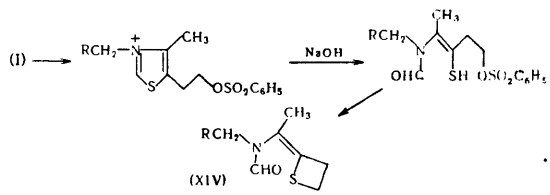
Thiamine is hydrolysed in alkaline media to thiol forms of the vitamin, which are derivatives of an unsaturated thiol. The properties of these derivatives are determined by the specific atomic grouping (XIII) present in all these compounds:



This grouping is liable to undergo various rearrangements, which occur under mild conditions. When the second valency of the sulphur forms part of a thiazole ring, ready closure of a perhydrofurothiazole ring is observed (as occurs with dihydrothiamine); if, however, a thiol group is adjacent to the double bond, dehydration to a thietan occurs. Formation of the four-membered ring is facilitated in arenesulphonic esters of thiamine, in which the atomic grouping

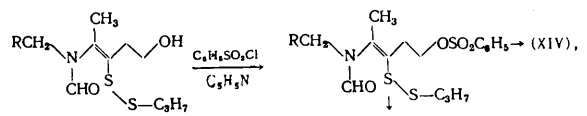


is readily broken between carbon and oxygen atoms. Therefore, in contrast to the monophosphoric ester of thiamine, the substituted sulphonates are extremely unstable, and in alkaline media undergo fundamental and irreversible changes. In alkaline solution thiamine is inactivated after the addition of only 1–3 drops of benzenesulphonyl chloride.[12] It has now been found that such treatment of the vitamin involves formation of a substance having the empirical formula $C_{12}H_{16}ON_4S$. This compound is not converted back into thiamine by cysteine, and hence does not contain a disulphide bond. It has the structure of an anhydride of the thiol form of the vitamin (XIV),[13] and has been called thiamine anhydride:



Thiamine anhydride, and also the corresponding sulphone formed by its oxidation with hydrogen peroxide, have practically no biological activity[14].

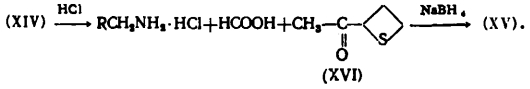
Careful treatment of thiamine chloride, or of alkyl thiamine disulphides in pyridine in the cold, with alkanesulphonyl or arenesulphonyl chlorides yields the corresponding sulphonates of the thiamine disulphides[15]:



which in alkaline alcoholic media are converted into thiamine anhydride (XIV).

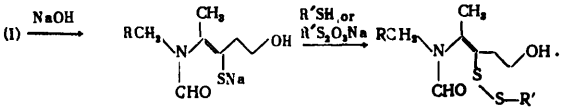
In order to elucidate the mechanism of this reaction, a study has been made of the behaviour of the benzenesulphonates of thiamine and thiamine disulphide in alkaline media. The former ester was found to be converted into thiamine anhydride even at pH 8, whereas more concentrated alkali is required for decomposition of the latter[16]. Treatment of β-deoxy-β-chloroethylthiamine with aqueous alkali gives the same result[17].

The thietan ring with the substituted *endo*-ethylene group is fairly stable: hydrolysis of thiamine anhydride with hydrochloric acid yields methyl 2-thietanyl ketone (XVI) which is reduced with sodium tetrahydroborate to 1-2′-thietanylethanol (XV):[18]

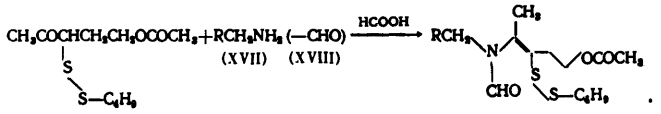


2. Unsymmetrical Disulphides of Thiamine

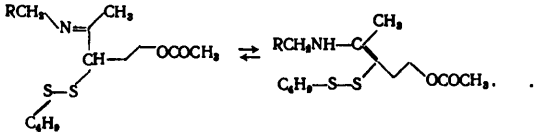
One of the most important reactions of the thiol form of vitamin B_1 is the formation of disulphide derivatives of thiamine. Treatment of thiamine with alkane-, arene-, and aralkane-thiols and with organic thiosulphates yields the corresponding alkyl, aryl, and aralkyl thiamine disulphides, which show vitamin activity[19]:



Another method of synthesising unsymmetrical thiamine disulphides consists in the condensation of 3-acetyl-3-butyldithiopropyl acetate with 4-amino-5-aminomethyl-2-methylpyrimidine (XVII) or its formyl derivative (XVIII), and treatment of the product with formic acid[20]:



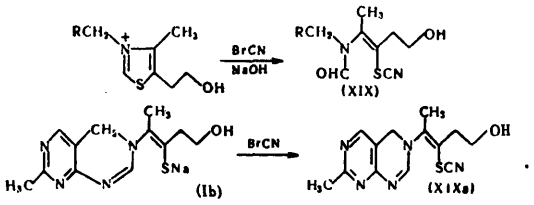
The above synthesis implies as a probable intermediate stage the tautomeric change:



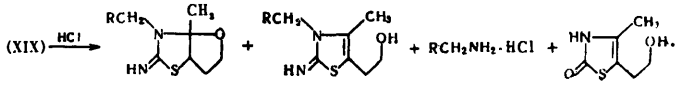
Alkylation of thiamine mononitrate with triphenylmethyl chloride and with derivatives of benzyl chloride yields benzyl thiamine sulphides[21].

3. Cyanothiamine and Its Reactions

The action on thiamine of cyanogen bromide in alkaline solution produces fundamental changes in the vitamin, the thiazole ring undergoing cleavage with formation of the so-called "cyanothiamine" (XIX),[22,26] which represents a new fat-soluble form of thiamine.[23] Also, the cyclic thiol of vitamin B_1 (Ib) is converted[24] by cyanogen bromide into the corresponding thiocyanate, which is termed "neocyanothiamine" (XIXa). This reaction has been investigated in detail, the influence of various substituents being studied, and has been shown to be fairly general for thiazolium salts containing various substituents in positions 3, 4, and 5:

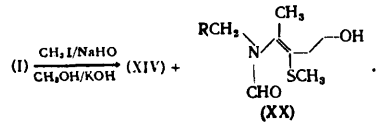


Hydrolysis of the unsaturated thiocyanate formed from 3-benzyl-5-2′-hydroxyethyl-4-methylthiazolium yields 3-benzyl-5,6,7,8-tetrahydro-2-imino-8-methylfuro[2,3-*d*]-thiazole, which has been isolated as the picrate. Similar treatment of "cyanothiamine" (XIX) produces a mixture of various compounds[25]:

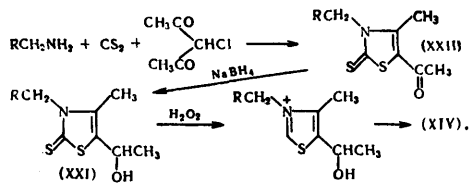


Heating "cyanothiamine" (XIX) with organic acids also results in cleavage with formation of a mixture of various acylated products[25]. Boiling (XIX) in butanol gives thiamine anhydride (XIV).[22]

A subsequent detailed investigation[27] of the inactivation of "cyanothiamine" (XIX) and its conversion into thiamine anhydride (XIV) has shown that methanolic alkali also effects this change, an *S*-methyl derivative of the B_1 thiol (XX) separating at the same time. This latter compound has been obtained also by the action of methyl iodide on the vitamin in alkaline solution, as well as by treatment with methanolic caustic potash:



It is interesting that the position of the hydroxyl in the hydroxyethyl group is of no significance for the formation of thiamine anhydride. The latter (XIV) is formed also from the 5-1′-hydroxyethylthiamine (XXI), which has been obtained from the corresponding 5-acetylthiazoline-2--thione (XXII):[27]



The presence of sulphur adjacent to the double bond is a necessary condition for the formation of a thietan ring.

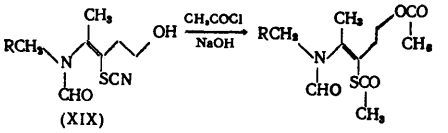
Thus, like other alkyl thiocyanates, 2-thiocyanatopentan-3-ol in methanolic alkali[27] merely yields disulphides[28]:

$$CH_3CH(SCN)CH_2CH(OH)CH_3 \rightarrow [CH_3CH(OH)CH_2CH(CH_3)-S-]_2.$$

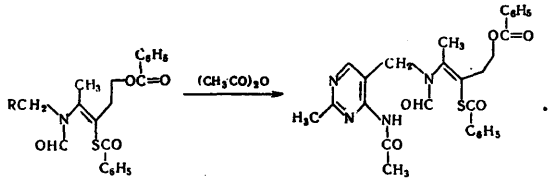
IV. ACYLATION OF THIAMINE AND ITS DERIVATIVES

Many *S*-acyl derivatives — *p*-nitrobenzoyl, *p*-chlorobenzoyl, *p*-toluoyl, phenylacetyl, cinnamoyl, furoyl, furylacryloyl, thenoyl, and butyryl — have been obtained by the acylation of thiamine *O*-monophosphate[29]. Dihydropyran acts on *S*-aroylthiamines to give ethers of the vitamin, *S*-aroyl-*O*-tetrahydropyranylthiamines[21].

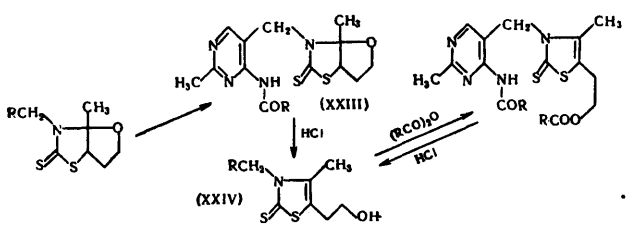
Acylation of "cyanothiamine" (XIX) with acid chlorides yields *OS*-diacylthiamines[30]:



The stability of the *S*-acyl derivatives of thiamine depends on the acidity of the medium and the nature of the acyl group. When *S*-benzoylthiamine is heated in an acid medium, migration of the benzoyl group is observed with formation of *O*-benzoylthiamine. This reaction goes better at pH 5. Aliphatic *S*-acylthiamines are less stable than the aromatic and heterocyclic derivatives, which may be explained by the inductive and steric effects of acylthiamines[31]. Acylation of *OS*-dibenzoylthiamine and *OS*-diacetylthiamine with acetic anhydride yields *N*-acetyl-*OS*-dibenzoylthiamine and *NOS*-triacetylthiamine respectively[32]. Other *N*-acyl derivatives have been obtained in a similar manner[33]. On the other hand, treatment of *S*-benzoylthiamine with succinyl anhydride has given *S*-benzoyl-*O*-succinylthiamine[34].

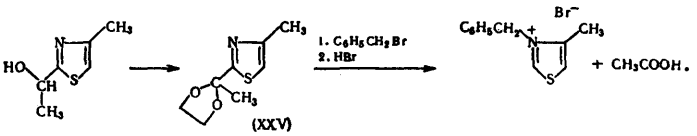


A study has been made of the acylation of one of the most important intermediates in the synthesis of thiamine, the 3-pyrimidinylmethylthiazoline-2-thione or so-called "thiothiamine" (XXIV).[35] However, such reactions cannot be used for the synthesis of biologically important *N*-acylthiamines, since *N*-acylthiazolinethiones are readily hydrolysed by dilute acid. Acyl derivatives of perhydrofurothiazolethione (XXIII) are equally readily hydrolysed by acids, the tetrahydrofuran ring being at the same time cleaved with the formation of "thiothiamine" (XXIV):



Nevertheless, the diethyl and diphenyl phosphates formed by the phosphorylation of "thiothiamine" (XXIV) are resistant to the action of hydrogen peroxide, and are readily converted into the corresponding substituted phosphates of thiamine[36]. It has also proved possible to phosphorylate *S*-benzoylthiamine, with the resulting synthesis of *S*-benzoylthiamine *O*-phosphoromorpholidates[37].

C_2-Acyl derivatives of thiamine have not yet been obtained owing to their instability[38]. Oxidation of 2-1′-hydroxyethyl-4-methylthiazole has given 2-acetyl-4-methylthiazole in the form of a dioxolan derivative (XXV), which is converted by benzylation and hydrolysis into 3-benzyl-4-methylthiazolium bromide:



In another case the extraordinarily unstable 2-acetyl-3,4-dimethylthiazolium system was obtained. 2-Benzoyl-3,4-dimethylthiazolium iodide, prepared from 2-benzoyl-4-methylthiazole and methyl iodide in dimethylformamide, decomposed into methyl benzoate and 3,4-dimethylthiazolium iodide on dissolution in methanol.

2-Benzoyl-3,4-dimethylthiazolium iodide was found to have a very high free energy of hydrolysis[39]. The value calculated for 2-acetylthiamine phosphate places this compound among other classic phosphates (ATP, etc.), while the presence of a labile bond in position 2 of 2-acylthiazolium allows us to speak of a new type of "high-energy bond".

V. THIAMINE–PROTEIN COMPLEXES

Thiamine forms stable complexes with several proteins, for example by precipitation on casein[40]. Ovalbumin and denatured milk protein with thiamine disulphide form thiamine itself and undialysable protein–thiamine complexes[41] having 90% of the activity of the vitamin.

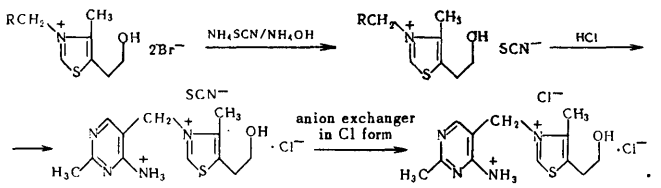
Further work has shown[42] that this complex has a disulphide structure, since the vitamin is liberated on treatment with cysteine or sodium thiosulphate.

The protein of soya-bean oil firmly retains thiamine after being frozen and then allowed to melt again[43]. The adsorption of various derivatives of thiamine — the hydrochloride, nitrate, thiocyanate, dihexadecyl sulphate, and dibenzoate — has been investigated. They are all found to combine firmly with the protein, and have been isolated after treatment with proteinase and Taka-Diastase and after acid hydrolysis of the adsorbate. After denaturation of a protein, its capacity for adsorption is affected by hydroxylamine solution; mercury *p*-chlorobenzoate does not affect this property. Hence it is concluded that the active centre in a protein which is responsible for combination with thiamine contains a carbonyl group. It is noteworthy that thiamine diphosphate also forms a quite stable complex with an apoenzyme. Although the affinity of thiamine diphosphate for carboxylase is 3.3×10^{-6}, the enzyme dissociates very slowly[4]. No other quantitative data have been published to characterise the bond between thiamine and a protein.

VI. DERIVATIVES OF THIAMINE

1. Salts and Esters of Thiamine

Much work has been done during recent years on the synthesis of various salts and derivatives of thiamine[44-60], and tens of derivatives of vitamin B_1 have been described, including various halides. Monosalts, including thiamine mononitrate, which has been extensively used in clinical practice[44], have been obtained by partial neutralisation to pH 6 of the chloride of thiamine hydrochloride, the so-called thiamine chloride, followed by salting out with appropriate salts. The mononitrate, together with other salts, can also be obtained by an ion-exchange method[61]. Thiamine bromide hydrobromide is first converted into thiamine thiocyanate by treatment with ammonium thiocyanate in ammonium hydroxide, and the product is dissolved in hydrochloric acid and passed through an anion-exchanger:



Chlorides and other salts of thiamine are obtained in this way.

A method has been described for converting vitamin B_1 bromide hydrobromide into the hydrochloride of the chloride which is based on the greater volatility of the alkyl bromides produced on treatment of the former with anhydrous hydrogen chloride in the lower aliphatic alcohols[62].

The hydrochlorides of thiamine bromide and iodide have been prepared by the action of concentrated hydrochloric acid on the thiamine halides followed by precipitation with acetone[52]. The sulphate[47] and also various alkane- and arene-sulphonates of thiamine[48-51] have been synthesised and studied. Thiamine sulphate has been obtained by treatment of the hydrochloride with chlorosulphuric acid[47].

Most of the substituted sulphonates are sparingly soluble in water. The following salts of thiamine have been prepared: the cyclohexylmethanesulphonate, mesitylenesulphonate, diphenylmethane-*pp'*-disulphonate, 2,2-diphenylpropane-*pp'*-disulphonate, 2,2-dibenzylpropane-*pp'*-disulphonate, 2,2',4,4',6,6'-hexamethylbiphenyl-3,3'-disulphonate, and naphthalene-1,5- and -2,6-disulphonates[54].

The salts formed by thiamine and dibenzylthiamine with cyclohexylsulphamic acid are fairly stable[51].

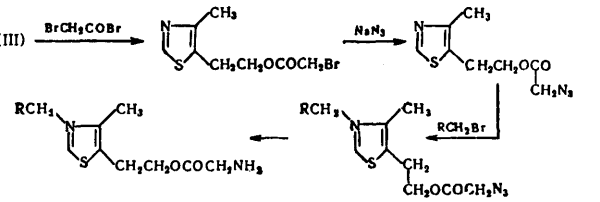
Thiamine di(hexadecylsulphonate), which is sparingly soluble in water, is more stable than thiamine chloride on heating, and can be successfully used for addition of the vitamin to bread and other foodstuffs.

Salts — the sulphate, fumarate, nitrate, chloride, bromide, iodide, oxalate, saccharinate, and di(hexadecylsulphonate) — have also been obtained by double decomposition of the Eosin–vitamin B_1 complex with the corresponding acids[53].

Various salts of thiamine with organic acids have been prepared — the monosaccharinate[57], disaccharinate[63], tannate[58], salicylate and various of its derivatives[59], and glycyrrhizate (the acid has been isolated from *Glycyrrhiza uralensis*[56]) — as well as thiamine derivatives of gibberellin[64], the dodecyl phosphate[45], and other salts such as the tetraphenylborate[46]. A coloured salt of thiamine with an acid sulphopyrazoline azo dye has been prepared[60].

Various esters of the hydrobromide and the hydrochloride of thiamine have been prepared — the octanoic, lauric, myristic, palmitic, stearic, succinic, and phthalic esters[65]. Animals readily assimilate them, especially the palmitic ester[17].

Attempts to prepare amino-acid and carbohydrate derivatives of thiamine are also of great interest. From 2-(4-methylthiazol-5-yl)ethyl azidoacetate and 4-amino-5-bromomethyl-2-methylpyrimidine has been obtained thiamine azidoacetate, reduction of which gives thiamine glycinate. Its phenylacetates have been synthesised in a similar manner[66].



Thiamine *S*-β-D-glucoside has been synthesised from *O*-benzoylthiamine hydrochloride and bromoacetyl-α-glucose[67].

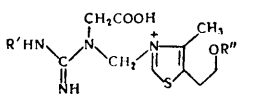
2. Derivatives of the Thiol Form of Thiamine

During recent years reports have appeared on the production of new types of vitamin B_1 preparations which are derivatives of the thiol form of thiamine. Several tens of unsymmetrical disulphides have been synthesised[68-76]. Among these, Japanese investigators have suggested as new vitamin preparations — propyl thiamine disulphide (a structural analogue of allylthiamine), tetrahydrofurfuryl thiamine disulphide, and also 8-(methyl 6-acetyldihydrothiooctanoate)thiamine disulphide[68]. These compounds have been synthesised by the methods described above.

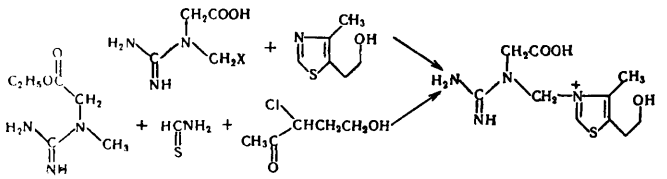
An effective new preparation, *S*-benzoylthiamine-*O*-monophosphoric ester of "cyanothiamine" (XIX).[30] Treatment of (XIX) and its *O*-benzoyl derivative with thiols yields the corresponding thiamine disulphides[75]. It has been established that allyl and propyl thiamine disulphides, *OS*-diacetylthiamine, and *OS*-dibenzoylthiamine are absorbed in the intestine more readily than is thiamine chloride, while propyl thiamine disulphide is able to maintain the highest vitamin B_1 level in the blood[77].

3. New Natural Compounds Closely Related to Thiamine

Two natural products have recently been isolated from Japanese garlic[78]. They resemble thiamine in their action, and have been termed scordinines A and B. They both contain what has been termed a thiamidine grouping



Like vitamin B_1, the scordinines contain thiazole rings, but the pyrimidine moiety has been replaced by a creatine grouping. The basic structure of the scordinines has been synthesised in two ways:

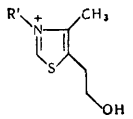


The two compounds differ only in the substituents R′ and R″, the structure of which has not been precisely established. It is known only that scordinine A, which is formed in garlic after several months of storage, contains a phosphatide.

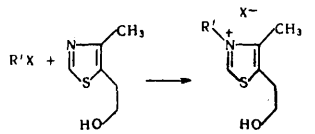
A new group of unsymmetrical pyrophosphates has been discovered, among them a thiamine diphosphate–3-acetamido-3,6-dideoxyhexose, which like the nucleoside sugar diphosphates, acts as a donor of glycosidic residues in the biosynthesis of the exopolysaccharide of *Xanthomons campestris* [79].

4. Analogues of Thiamine

Investigation of the relation between structure and biological activity in thiamine derivatives long ago led to the synthesis of pyrithiamine and other substances possessing the properties of antivitamins. The systematic synthesis of various analogues of thiamine allowed several links to be noted between structure and biological activity. In all cases the analogues were built up according to the principle of so-called "isosteric inhibition", the synthesised analogue of general formula

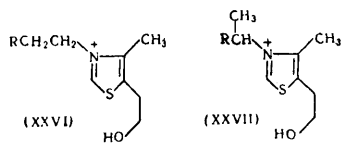


being similar in volume and configuration to the natural vitamin. In this way changes were introduced into the pyrimidine portion of the molecule. All these analogues were usually synthesised by the reaction



where R′ is a heterocyclic radical.

2-Trifluoromethylthiamine proved to be a vitamin inhibitor and possessed interesting biological properties [80]. For example, it suppressed the development of leukaemia and the growth of a transplanted carcinoma in mice on a diet deficient in vitamin B_1.

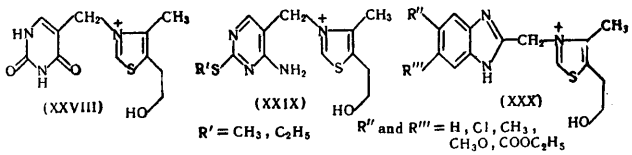


Investigation of the catalytic properties of the synthetic thiamine homologues (XXVI) and (XXVII) on a model system reproducing the synthesis of acetoin (V) showed that the former has 67%, and the latter (XXVII) 5%, of the activity of thiamine [81]. None of the homologues possessed vitamin activity in microbiological tests with *Kloeckera brevis*.

6-Methylthiamine had about one-third of the activity of thiamine [82], while other results gave its activity as 18% of the latter [83].

A study of derivatives of vitamin B_1 in which the 2-methyl group had been replaced by ethyl, methoxymethyl, 2′-ethoxyethyl, phenoxymethyl, and 1′-bromoethyl groups showed most of them to be inactive in reactions involving decarboxylation. The only exceptions were 2′-ethoxyethylthiamine, whose activity in the decarboxylase reaction was low, and methoxymethylthiamine, which behaved as an antivitamin [84].

Heterocyclic analogues of thiamine have been synthesised — 3-(1,2,3,4-tetrahydro-2,4-dioxopyrimidin-5-ylmethyl)thiazolium [85] (XXVIII) derivatives, alkylthiopyrimidine analogues such as Methioprim (XXIX), [86] and also benzimidazole [87] analogues (XXX):



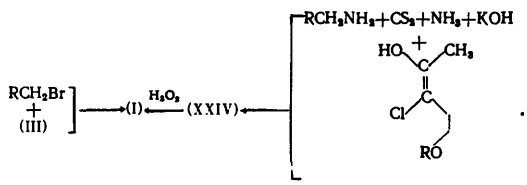
It must be noted that the synthesis of analogues on the principle of isosteric inhibition, which in many cases has proved so effective in the search for drugs, has not yet given any practical result in the thiamine field. This is primarily an indication of the highly specific chemical structure of the vitamin.

Nevertheless, the discovery of the natural antibiotic bacimethrin (from *Bacillus megaterium*), which is active against yeasts and bacteria, and the establishment of its structure as identical with 4-amino-5-hydroxymethyl-2-methoxypyrimidine [88], give grounds for hoping that practical advances may be expected in this field too.

VII. DEVELOPMENT OF INDUSTRIAL METHODS FOR SYNTHESISING VITAMIN B_1

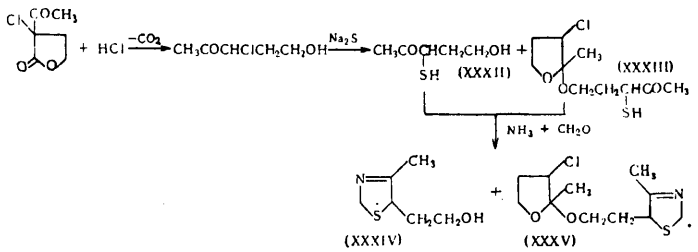
Various syntheses of thiamine have already been described in detail [89]. Two main processes are used in various countries for the production of vitamin B_1 — (i) from 5-bromomethylpyrimidine and 5-2′-hydroxyethyl-4-methylthiazole and (ii) *via* 3-(4-amino-2-methylpyrimidin-5-ylmethyl)-5-2′-hydroxyethyl-4-methylthiazole-2-thione (XXIV) (the so-called "thiothiamine"). The history of the appearance of the second industrial method for synthesising vitamin B_1 in Japan is linked with the struggle between Japanese and American pharmaceutical firms for the market. Although the large-scale production of vitamin B_1 has been organised in the USSR too, no final choice has yet been made of a particular method of synthesis. New

research on the synthesis of this vitamin is developing these two traditional processes.

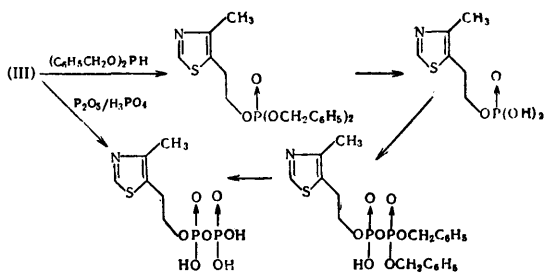


1. Synthesis from 5-2′-Hydroxyethyl-4-methylthiazole

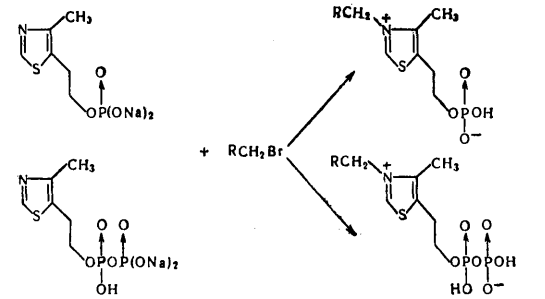
In a new method of synthesising the thiazole component of thiamine[90], α-acetyl-α-chloro-γ-butyrolactone is treated with concentrated hydrochloric acid to give 3-chloro-5-hydroxypentan-2-one, which with alcoholic sodium sulphide solution yields a mixture of 5-hydroxy-3-mercaptopentan-2-one (XXXII) and 5-(3-chlorotetrahydro-2-methylfur-2-yloxy)-3-mercaptopentan-2-one (XXXIII). Treatment of this mixture with paraformaldehyde and ammonia together with hexamethylenetetramine gives a mixture of 2-(4-methyl-Δ³-thiazolin-5-yl)ethanol (XXXIV) and the corresponding tetrahydrofuryl ether (XXXV):



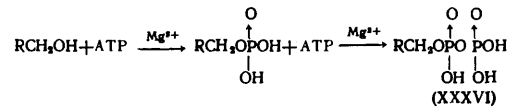
A new method has recently been described for obtaining thiamine phosphates[92], which supplements the well-known processes consisting essentially in treating thiamine with pyrophosphoric acid and then separating the phosphorylation products on chromatographic columns[91] to obtain the monophosphate and the diphosphate (TMP and TDP). 2-(4-Methylthiazol-5-yl)ethanol (III) is first phosphorylated in various ways:



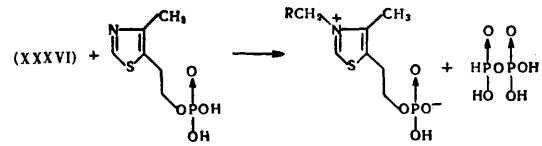
and the resulting monophosphoric and diphosphoric esters of thiazolylethanol are condensed with 4-amino-5-bromomethyl-2-methylpyrimidine to give high yields of TMP and TDP:



This method of synthesising thiamine phosphates resembles the biosynthesis of thiamine in many microorganisms. An enzyme present in cell-free extracts of yeasts has been found to catalyse condensation of the pyrimidine and thiazole moieties of thiamine[93]. This enzyme is activated by ATP. It is accepted[94] that the principal intermediate in the biosynthesis of thiamine is 5-(4-amino-2-methylpyrimidin-5-yl)methyl diphosphate (XXXVI). The main mechanism in the biosynthesis of thiamine involving this compound is represented by the following sequence of reactions: 4-amino-5-hydroxymethyl-2-methylpyrimidine is phosphorylated twice by means of ATP:



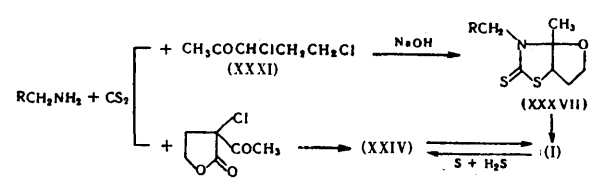
The resulting diphosphate reacts with the thiazolylethyl monophosphate, which itself has been formed by the phosphorylation of 2-(4-methylthiazol-5-yl)ethanol. This reaction yields TMP, and hydrolysis of the phosphoric ester bond yields thiamine:



Several methods of synthesising ^{35}S-labelled thiamine have been described which represent repetitions of various previously known processes[95,96].

2. Synthesis of Vitamin B_1 *via* "Thiothiamine"

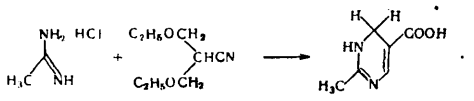
Various methods have been described for obtaining the thiazolinethione "thiothiamine" (XXIV).[97] Condensation of 4-amino-5-aminomethyl-2-methylpyrimidine (XVII) and carbon disulphide with 3,5-dichloropentan-2-one (XXXI) leads to the formation of 3-(4-amino-2-methylpyrimidin-5-yl)methyl-2,3,7,8-tetrahydro-4-methylfuro[2,3-*d*]thiazolidine-2-thione (XXXVII), oxidation of which gives thiamine[98,99]:



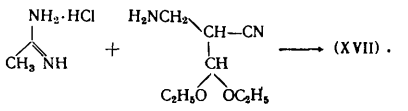
Treatment of "thiothiamine" (XXIV) with hydrogen peroxide in the presence of carbonates of the alkaline earth metals[100] leads to the formation of monosalts of thiamine — the monochloride, monoiodide, mononitrate, and monothiocyanate.

The conversion of "thiothiamine" into thiamine is reversible: if thiamine is heated with sulphur or with hydrogen sulphide, "thiothiamine" is formed[101].

In the subsequent improvement of the method of synthesis *via* "thiothiamine", great attention has been paid to various alternative syntheses of 4-amino-5-aminomethyl--2-methylpyrimidine (XVII) from derivatives of β-alkoxy- or β-amino-propionitriles. Bisethoxymethylacetonitrile reacts with acetamidine to form 3,4-dihydro-2-methylpyrimidine-5-carboxylic acid[102]:



The pyrimidine (XVII) has been obtained in about 60% yield from α-aminomethyl-ββ-diethoxypropionitrile and acetamidine[103]:



A similar result has been obtained by heating β-acetoxy--α-ethoxymethylenepropionitrile with acetamidine in an autoclave at 140–150°, and hydrolysing the product with a 10% solution of alkali[104].

VIII. MECHANISM OF THE ACTION OF VITAMIN B_1

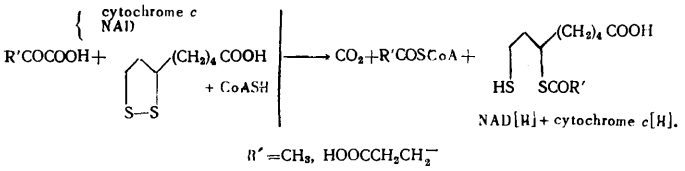
Study of the reactions of thiamine with aldehydes and keto-acids has revealed very important new properties of the vitamin. Thiamine and its phosphoric esters can effectively catalyse reactions of the aldol condensation type. These observations have finally enabled the mechanism of the biological action of vitamin B_1 to be understood.

In the organism thiamine undergoes phosphorylation, and in the form of the diphosphoric ester takes part in many biocatalytic processes. Thiamine pyrophosphate — or more correctly thiamine diphosphate (TDP) — forms part of many enzymes, in which it acts as prosthetic group or coenzyme, being quite firmly combined with the apoenzyme, a protein[105].

More than ten different enzymes are now known in which TDP has been shown to act as coenzyme[106], among them being enzymes or enzyme systems which effect the decarboxylation of pyruvic acid or other keto-acids, as well as enzymes which catalyse metabolic reactions of carbohydrates of the aldol synthesis or reverse aldol type. They include:

(1) α-Carboxylase, which effects the decarboxylation of α-keto-acids to the corresponding aldehydes and carbon dioxide:

(2) Various pyruvic acid and α-ketoglutaric acid dehydrogenases (oxidases), whose effect is to decarboxylate and oxidise these substrates. The role of acceptors of hydrogen and acyl groups (the role of cosubstrates and oxidation coenzymes) in these reactions is filled by lipoic acid, nicotinamide-adenine dinucleotide (NAD), cytochrome *c*, and coenzyme A:



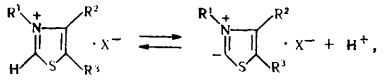
(3) A group of enzymes which effect reactions that are the reverse of the aldol condensation, for example phosphoketolase.

(4) Enzymes which catalyse aldol synthesis, among them being a transketolase from yeasts, which effects the formation of sedoheptulose 7-phosphate and glyceraldehyde 3-phosphate from xylulose 5-phosphate and ribose 5-phosphate. This group of enzymes includes an acetoin-forming complex from *Aerobacter aerogens* and a glyoxylic acid carboligase.

Although the participation of TDP in decarboxylation and other reactions of α-keto-acids has now been known for more than a quarter of a century[107,108], its mechanism remained obscure until recently. Many different hypotheses were put forward, supported to varying extents by chemical models, but none of them received experimental confirmation in the study of biological systems.

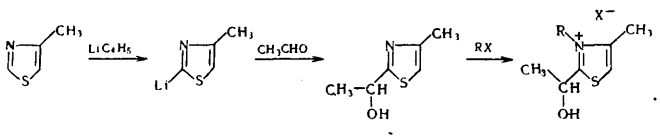
Breslow[109] has suggested a model general mechanism for the action of thiamine which combines two processes, decarboxylation of the keto-acid and an acyloin condensation. The role of cyanide, which catalyses the acyloin condensation, is to form a reactive intermediate carbanion with the aldehyde, which in turn reacts with a second molecule of the aldehyde to give the acyloin.

Thiazolium derivatives also are capable[110] of giving reactive intermediate carbanions, to which pyruvic acid adds on readily. Study of the isotopic exchange of deuterium with thiazolium has shown the existence of the tautomeric equilibrium[111]

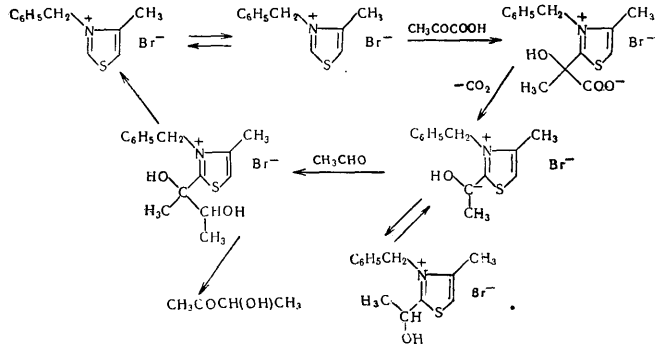


since 3,4-dimethylthiazolium and 3-benzyl-4-methylthiazolium bromides readily exchange hydrogen in position 2 of the thiazolium ring for deuterium in heavy water. The carbanion readily adds on pyruvic acid, the mechanism of this reaction being analogous to the first stage in the acyloin condensation. Decarboxylation yields the intermediate 1-thiazol-2′-ylethanol.

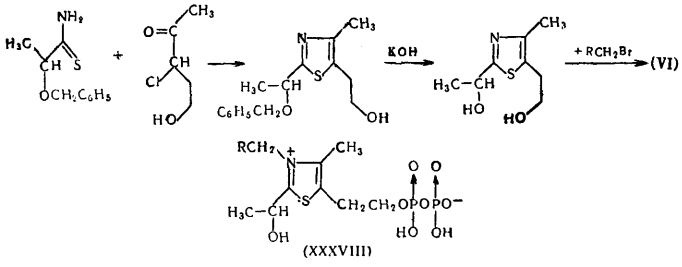
Such derivatives have been prepared by an independent method[112] involving organolithium compounds:



3-Benzyl-2-1′-hydroxyethyl-4-methylthiazolium bromide has been prepared in this way and proves to be an active catalyst for the synthesis of acetoin from pyruvic acid. The mechanism of this reaction has been represented by the scheme



The benzyl group has been found to play an important part, since 2-1′-hydroxyethyl-3,4-dimethylthiazolium bromide possesses far weaker catalytic properties. This view is supported by the observation that, at 25° and pH 5.37, deuterium exchange is three times as rapid with the 3-benzyl derivative than with the 3-methylthiazolium salt. This observation throws light on the role of the pyrimidine moiety of thiamine: it is obviously necessary to produce the electronic interaction which will facilitate formation of the carbanion. The great effectiveness of thiamine is thus explained by the greater electrophilic effect of the pyrimidinyl than of the phenyl group. "2-Hydroxyethylthiamine", *i.e.* the hydrochloride of DL-3-(4-amino-2-methylpyrimidin-5-yl)-methyl-2-1′-hydroxyethyl-5-2″-hydroxyethyl-4-methylthiazolium chloride[112], possesses similar properties, and replaces thiamine in the growth of microorganisms on nutrient media. Its synthesis leaves no doubt that the hydroxyethyl group is located at position 2 in the thiazole ring:

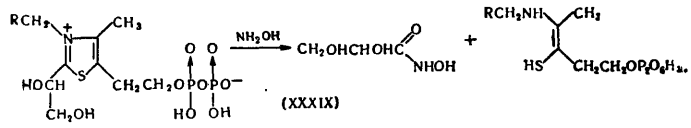


From a mixture of TDP and acetaldehyde was then isolated "2-1′-hydroxyethylthiamine diphosphate" (XXXVIII).[5] Labelled (XXXVIII) was prepared from acetaldehyde labelled at both carbon atoms, and was used subsequently in biochemical investigations. This compound was found to fill the role of "active acetaldehyde", the existence of which had been suggested previously.

Labelled 2-1′-hydroxyethyl-TDP has been shown[5] to be an intermediate in the formation of acetaldehyde by wheat-germ carboxylase, in the formation of acetoin by enzyme preparations obtained from *Aerobacter aerogens*, and in the formation of acetate by an artificial system simulating pyruvic acid oxidase.

The use of labelled bishydroxyethyl-TDP (XXXIX), prepared from labelled formaldehyde and TDP as well as from hydroxypyruvic acid and TDP in the presence of heart-muscle pyruvate oxidase[113], in reactions with ribose 5-phosphate catalysed by baker's yeast transketolase has provided a demonstration, based on the presence of the tracer in the resulting sedoheptulose 7-phosphate, of the role of (XXXIX) as an active intermediate in this reaction too[115].

The structure of 2-dihydroxyethyl TDP, "active glycollaldehyde" (XXXIX) has been proved by the hydroxamic reaction[114]:



Elucidation of the role of hydroxyethyl derivatives of thiamine enables discussion of enzyme reactions involving TDP to be based on a single mechanism.

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Knowledge of the mechanism underlying the action of thiamine yet again confirms the remarkable fact that all biochemical processes have their analogues in non-enzymatic reactions of organic compounds, the laws of which remain in force for enzyme reactions too.

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THE KINETICS OF ION EXCHANGE ON SULPHONATED CATION EXCHANGERS

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A solution to the problem of creating high-quality ion exchangers, as well as a rational approach to the selection of optimum operating conditions for ion-exchange units and the regeneration of ion exchangers, is only possible with a detailed knowledge of both equilibrium and kinetic data.

However, while many studies have been concerned with the statics of ion-exchange processes the kinetics of ion exchange and the kinetic properties of ion exchangers have been investigated to a considerably lesser extent. Of the reviews which have appeared recently, three [1,2,3] should be noted in which problems of ion-exchange kinetics have been partially discussed. In Helfferich's detailed monograph [3], where the theory of ion-exchange processes is set out fairly fully, little attention is paid to experimental data on ion-exchange kinetics and, in particular, on the coefficients of diffusion and self-diffusion in ion exchangers; in addition, the investigations by Soviet authors are not sufficiently reflected. In the present review we would like to remedy this omission and pay particular attention to reviewing the theoretical and experimental information on the kinetics of ion exchange in the processes of self-diffusion, the diffusion of microcomponent ions, complete exchange, and the exchange of large ions on strongly acid cation exchangers. In presenting the information we shall not refer back to the problems set out in Helfferich's book.

I. FUNDAMENTAL PROBLEMS IN THE THEORY OF ION-EXCHANGE KINETICS

If an ion A from a solution replaced an ion B in an ion exchanger then the exchange process takes place primarily in the following stages: the diffusion of the ion A through the layer of liquid adjacent to the ion-exchange particle, the transfer of the ion A from the solution phase to the ion-exchanger phase, the diffusion and exchange of the A and B ions within the ion exchanger, the transfer of the B ion from the ion-exchanger phase to the solution phase, and diffusion of the B ion through the layer of solution adjacent to the ion-exchange particle. It should be borne in mind that due to the necessity for preserving the electroneutrality of the solution, the transfer of the ions during diffusion is balanced by a counter flow.

In the first stages of investigating ion-exchange kinetics (up to approximately 1950) some authors attempted to use the concept of "the order of reaction" of the ion-exchange process to explain the experimental results, assuming the

existence of a chemical mechanism in ion-exchange processes. Nowadays, however, it is generally considered that chemical stages are not the rate-determining ones in all the ion-exchange processes on sulphonated cation-exchangers so far investigated, and that the exchange is a series of purely physical processes, those of transfer and diffusion. It is considered that the rate-determining steps are either the diffusion of ions in solution or diffusion within the ion-exchanger particles. In some cases both these processes affect the rate of exchange.

When analysing the kinetics of ion exchange it is usually assumed that mixing leads to an instantaneous levelling out of the concentration within the bulk of the solution but there is a thin film of immobile solution in the region of the solid surface where transfer is achieved only by diffusion. Of course, the true state of affairs is much more complicated and requires the solution of complex hydrodynamic equations but, nevertheless, the model of a film of finite thickness has been found to be extremely effective in explaining the series of processes. As the flim thickness is not a physical quantity but a fictitious one, rather, it is impossible to determine it by a direct method. From data on the rate of dissolution of solids and investigations on the kinetics of electrode processes, film thicknesses of the order of 10^{-2}–10^{-3} cm and even $\sim 10^{-4}$ cm at higher flow rates are obtained; similar values for film thickness are obtained from studies of the kinetics of ion exchange for film diffusion.

One of the characteristic features of a film diffusion exchange mechanism is the dependence of the rate of exchange on the rate of filtration of a solution or the intensity of agitation.

Diffusion within the particle will be the rate-determining process when the transfer of ions to the surface of the particle takes place more rapidly than their transfer into the solid phase. In practice the following factors will contribute to this: (a) a high concentration of the ion being exchanged in solution; (b) an effective agitation or rapid flow of the solution; (c) a large particle size; (d) a high degree of cross-linking or large and multicharged ions.

The determination of the transition from film diffusion kinetics to particle diffusion kinetics is of particular interest. Working with sulphonated cation exchangers of an average degree of cross-linking and at fairly high flow rates, Boyd *et al.*[4] showed that the rate of ion exchange in 0.1 M and more concentrated solutions is determined by particle diffusion, and in 0.001 M and less dilute solutions by film diffusion. According to the theory of Adamson and Grossman[5,6], the rate-determining step in the exchange process is film diffusion for values of the parameter $D_S R/D_i \delta k$ appreciably less than unity while for values of this parameter greater than unity it is particle diffusion. Here the parameters D_S and D_i are the diffusion coefficients in the solution and in the ion exchanger respectively, R is the radius of the particle, δ the film thickness, and k the diffusion coefficient for the diffusing particles (*i.e.* $[A]/[A_S]$). Helfferich[3] defined the form of this parameter somewhat more precisely as

$$\frac{cD_s R}{aD_i \delta}(5 + 2K_B^{\Delta}),$$

where K_B^{Δ} is the concentration equilibrium constant, a the capacity of the ion exchanger, and c the concentration of the outer solution. It should be pointed out that all these relationships which define the region of transition from film diffusion to particle diffusion kinetics are approximate in nature and are mainly used for average rates of exchange.

When analysing experimental data, as further consideration will show, it must be remembered that for a film diffusion mechanism of ion exchange (this relates primarily to the processes of self-diffusion and the diffusion of micro-component ions) the relative rate of exchange is inversely proportional to the radius of the ion exchanger particle and for a particle diffusion mechanism it is inversely proportional to the square of the radius in the first stages of exchange. If the rate-determining step of the exchange were to be a chemical reaction, then the rate of exchange on ion exchangers should not depend on their grain size.

Considerable mathematical difficulties arise in expressing the diffusion process in ion exchange, some of which have still not been overcome at the present time.

From the point of view of their mathematical description the main diffusion processes of ion exchange can be divided into five cases: (1) diffusion through the film of solution adjacent to the particle of ion exchanger, with a constant concentration in the outer solution; (2) diffusion through the film with a variable concentration in the outer solution; (3) diffusion within the ion-exchanger particle at a constant concentration in the outer solution; (4) diffusion within the ion-exchanger particle with a variable concentration in the outer solution; and (5) diffusion processes taking place simultaneously both in the film of solution and in the ion-exchanger particle.

As sulphonated cation exchangers mostly consist of spherical particles we shall only deal with the case of spherical symmetry.

In the mathematical treatment of the experimental results it is assumed that the thickness of the diffusion film of solution is constant, although there have been attempts[7] to take account of the asymmetry of the film thickness in relation to the flow of solution. We shall use the following general system of notation in our subsequent account:

c = the concentration of the outer solution, mg-equiv. cm^{-3},
c_0 = the initial concentration of the outer solution,
δ = diffusion film thickness, cm,
D_S = diffusion coefficient in the solution, $cm^2\ s^{-1}$,
D_i = diffusion coefficient within the ion-exchanger particle, $cm^2\ s^{-1}$,
R = radius of ion-exchanger particle, cm,
a = capacity of the ion exchanger, mg-equiv. cm^{-3},
F = fractional attainment of equilibrium,
n = mole fraction of the displacing ion in the solution,
N = mole fraction of the displacing ion in the ion exchanger,
$1 - n$ = mole fraction of the ion being displaced, in the solution,
$1 - N$ = mole fraction of the ion being displaced, in the ion exchanger,
v_S = volume of solution,
v_i = volume of ion exchanger,
t = time, s.

For isotopic exchange at a constant concentration in the outer solution, when the transfer through a film can be characterised by a single diffusion coefficient, the equation

$$F = N = 1 - \exp\left(-\frac{3D_s c_0}{R\delta a}\, t\right) \qquad (1)$$

has been derived[4].

It is not difficult to derive also the relationship for the more general case, where $K \neq 1$. Equating the diffusion flow through the film

$$4\pi R^2 D_s \frac{c(n_0 - n)}{\delta} dt$$

to the change in the content of the ion being displaced in the ion-exchange particle

$$\frac{4\pi R^3}{3} a \, dN,$$

and taking into account the establishment of equilibrium at the phase boundary

$$\frac{N}{1-N} = K \frac{n}{1-n},$$

we obtain the following differential equation

$$\frac{3D_s c_0}{\delta R a}\left(n_0 - \frac{N}{K-(K-1)N}\right) = \frac{dN}{dt}. \quad (2)$$

Integrating this equation for complete exchange, *i.e.* taking into account that $n_0 = 1$ and $N = 0$ at $t = 0$, gives the final equation

$$\frac{3D_s c_0 K}{\delta R a} \cdot t = -\ln(1-N) + (K-1)N. \quad (3)$$

It is not possible to find $N(t)$ from Eqn. (3), but the results of certain numerical calculations based on Eqn. (3), shown in Fig. 1, give a graphical representation of the effect of the equilibrium constant on the nature of the film diffusion kinetics of exchange. At $K = 1$ Eqn. (3) is transformed into Eqn. (1). D_S in Eqn. (3) should be taken as the diffusion coefficient of the electrolyte.

Adamson and Grossman[5,6] have proposed more complex equations than Eqn. (3) to describe the kinetics. These equations contain the different diffusion coefficients of the exchanging ions, and the electric charge balance in the flow is not introduced. Therefore the equations they suggest are not consistent and their unwieldiness is unjustified.

Taking the hydrogen–caesium and sodium–caesium exchange reactions as an example, these authors[6] established a linear relationship between $[\ln(1 - N)]/t$ and N/t. In a later paper[8] an attempt was made to take account of the effect of the diffusion electric potential on film diffusion kinetics. Starting from the Nernst–Planck equation

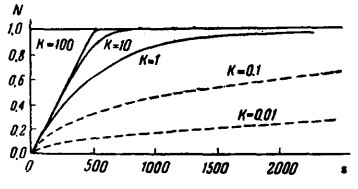

Fig. 1. Calculated curves for complete exchange at constant concentration in the external solution (at $D_i = 2 \times 10^{-5}$ cm^2 s; $\delta = 6 \times 10^{-4}$ cm; $R = 0.05$ cm; $a = 2$ mg-equiv. cm^{-3}; $c_0 = 2 \times 10^{-3}$ mg-equiv. cm^{-3} and different values of the equilibrium constant K).

and neglecting any selectivity in the exchange ($K = 1$), the authors obtained the following equation:

$$\ln\left\{\frac{y(t)-1}{(D_A/D_B)^{1/3}-1}\right\} + \frac{1}{2}\left[y^2(t) - \frac{D_A}{D_B}\right] + y(t) - \left(\frac{D_A}{D_B}\right)^{\frac{1}{3}} = -\frac{3D_A c}{R\delta a}t, \quad (4)$$

$$y(t) = [D_A N + D_B(1-N)]/D_B.$$

If the exchange process takes place through a film between the ion exchanger and a solution of limited volume, then for isotopic exchange ($D_{SA} = D_{SB}$ and $K = 1$), applying Eqn. (3):

$$F = \frac{N(0) - N(t)}{N(0) - N(\infty)} = 1 - \exp\left[-\frac{3D(v_i a + v_s c)}{R\delta a v_s} t\right]. \quad (5)$$

For other cases of exchange in a limited volume of solvent it is possible to obtain differential equations representing the process, but their solution will be fairly complicated and hardly suitable for practical application.

The process of diffusion exchange in a particle for constant concentration of the outer solution is represented by the well-known solution to the equation for diffusion in a sphere:

$$F = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{\exp(-n^2 B t)}{n^2}; \quad B = \frac{\pi^2 D_i}{R^2}. \quad (6)$$

When carrying out experiments the degree of exchange F, which is dependent on time, is determined from the results of the measurements. Then from a tabulation in the literature[4], which gives the variation of F with Bt, the value of B for corresponding values of F and t are found and the diffusion coefficient D_i found from the expression $D_i = BR^2/\pi^2$.

In the case of exchange with a limited volume of solution, the concentration of the electrolyte solution is a variable in the film diffusion kinetics, and when solving the diffusion equation account should be taken of the boundary condition which expresses the conservation of the total number of ions:

$$\frac{dc}{dt} = \frac{4\pi R^2 D_i}{v_s}\left[\frac{\partial(aN)}{\partial r}\right], \quad (7)$$

where $r = R$.

The solution of the corresponding problem for thermal conductivity has been given by Patterson[9]:

$$F = 1 - \frac{2}{3w}\sum_{n=1}^{\infty}\frac{e^{-\lambda_n^2 \tau}}{1 + \lambda_n^2/9w(1+w)}, \quad (8)$$

where $w = k(v_i/v_s)$, k is the sorption coefficient, $\tau = D_i t/R^2$ a dimensionless parameter, and λ_n are the roots of the transcendental equation

$$\lambda \coth \lambda = 1 + \frac{\lambda^2}{3w}.$$

Eqn. (8) is applicable for $\tau > 0.1$. For $\tau < 0.1$ the degree of exchange should be determined from the expression

$$u' \simeq \frac{1}{\alpha - \beta}\{\alpha e^{\alpha^2 t}(1 + \operatorname{erf}\alpha\sqrt{\tau}) - \beta e^{\beta^2 t}(1 - \operatorname{erf}\beta\sqrt{\tau})\}, \quad (9)$$

where α and β are the roots of the equation $x^2 + 3\omega x - 3\omega = 0$.

From Eqn. (9), F is determined by means of the relationship

$$F = \frac{1-u'}{1 - 1/(w+1)}. \quad (10)$$

For the practical use of Eqns. (8), (9), and (10) the variation of F with τ must first be plotted for values of ω corresponding to the experimental conditions, and then τ and the corresponding D_i found from the experimentally determined values of $F(t)$ (*cf.* Fig. 2). This method of determining the diffusion coefficient was successfully used in the studies of Soldano *et al.*[10,11,12]

As with the electrolyte solution, an electrical diffusion potential is produced within the ion-exchanger particle during the exchange of ions of different mobilities. In some papers[13,14,15] the diffusion processes of complete exchange in ion exchangers were examined, taking into account the effect of an electric field. The diffusion current can be expressed by the relationship

$$I = kTB_2\frac{da}{dx} + BEzea, \qquad (11)$$

where B is the mobility of the ion in the ion exchanger, ze the ionic charge, E the potential of the electric field produced in the ion exchanger during the exchange of ions of different mobilities, and a the concentration expressed in g-equiv.

Taking into account the conservation of overall electroneutrality, the effective diffusion coefficient for complete exchange will be

$$D_{eff} = \frac{D_1 D_2 (a_1z_1 + a_2z_2)}{D_1a_1z_1 + D_2a_2z_2}, \qquad (12)$$

where $D_1 = kTB_1$ and $D_2 = kTB_2$. Here D_1 and D_2 are functions of the composition of the ion exchanger at a given point, their form being unknown, although limiting values can readily be determined.

The expression given for the effective diffusion coefficient is approximate, as it does not take into account the activity coefficients of the ions in the ion exchanger, the variations in its swelling, and the transfer of water. An examination of the expression for the effective diffusion coefficient shows that in the initial and final stages of exchange, when one of the exchanging ions is present in the ion exchanger in low amounts (a microcomponent ion), D_{eff} is determined by the mobility of this ion.

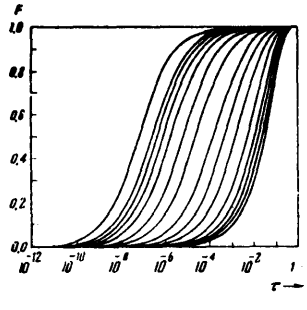

Fig. 2. Variation of F with τ for different values[9] of ω (from left to right, curves corresponding to ω = 1000; 500; 400; 300; 200; 100; 50; 20; 10; 5; 2; 1; 0.5; 0.2; 0).

The greatest complexity arises in a mathematical description of the processes of complete exchange, when the rate of the process is determined simultaneously by diffusion through the film of solution and by diffusion within the particle of ion exchanger.

Pouchlý and Erdös[16-18] examined the kinetics of adsorption from solutions, taking account of particle diffusion and film diffusion for the case of linear sorption isotherms. Even assuming a linear sorption isotherm, however, fairly unwieldy expressions are obtained for the rate of the exchange process.

Another paper[19] gives a mathematical relationship between τ, the average period of adsorption of ions from particles, the coefficients of particle and film diffusion, and other quantities which determine the rate of the ion-exchange process. For spherical particles this relationship has the form

$$\bar{\tau} = \frac{R^2}{15D_i} + \frac{R\delta\gamma}{3D_s}, \qquad (13)$$

where γ is the sorption coefficient referred to 1 cm³ and the other symbols are given above. $\bar{\tau}$ denotes the mean time of desorption from the particle of the ion exchanger and in practice is defined as:

$$\tau = \int_0^\infty \left[1 - \frac{A(t)}{A(\infty)}\right] dt,$$

where $A(t)$ and $A(\infty)$ are the quantities of ions in a spherical particle at a given moment t and $t = \infty$ respectively. It is assumed that at $t = 0$, the ions are uniformly distributed throughout the volume. This integral can be readily solved graphically from the experimentally determined values of $A(t)$. In particular, the relationship (13) enables D_i to be found from the experimentally determined value of τ and the known values of D_s and δ. For very large particles and low values of γ and δ (highly concentrated solutions and high flow rates), Eqn. (13) enables the diffusion coefficient of the ions in the ion exchanger to be determined at once.

The sharpness in the chromatographic separation of different ions depends on the elution of the zone containing these ions. For a linear sorption isotherm and an infinitely high rate of exchange, the chromatographic zones are not eluted; elution is the result of a finite rate in the diffusion processes. From a practical point of view ion-exchange kinetic data can be used for estimating the degree of elution of the chromatographic zones. The same applies to the opposite problem, *viz.* the determination of the kinetic characteristics of the exchange process from the elution of the chromatographic zones.

The displacement and elution of the zones in a chromatographic column containing the ions of one of the elements being separated in microquantities may be represented by the following equation:

$$\frac{(\Delta\bar{v})^2}{v} = \frac{2R^2u}{15D_i} + \frac{2\Gamma\delta u}{S_s\rho D_s} + \frac{2Q^2D_l l}{u}, \qquad (14)$$

where $\bar{v}$ is the average volume of eluant required to transfer an ion through the column, $(\Delta\bar{v})^2 = \overline{(\bar{v} - \bar{v})^2}$ the mean square fluctuation of v, u the volume flow rate of the solution through the column, D_l the diffusion coefficient of ions, dependent on the longitudinal mixing of the solution in the column, Γ the adsorption coefficient referred to 1 cm³ of the granular layer, $S_s\rho$ the surface area of 1 cm³ of the granular layer, and Q the cross-sectional area of the column.

If it is assumed as an approximation that $\delta \simeq 1/u$ and the effect of longitudinal mixing is neglected, then Eqn. (14) may be written as

$$\frac{(\Delta\bar{v})^2}{v} = i + bv,$$

where

$$i = \frac{2cT}{S_{sp}D_s}; \quad b = \frac{2R^2}{15D_i}. \qquad (15)$$

The relationship (15) is also approximately true in those cases where the role of film diffusion is low. Thus, with these assumptions $(\Delta\bar{v})^2/v$ is a linear function of velocity. From the slope of the straight lines which give the variation of $(\Delta\bar{v})^2/v$ with the rate of flow through the column, and using the expression for b, the value of the diffusion coefficient can be readily found. In those cases where the role of the processes in solution appreciably affects the elution of the chromatographic zones, the contribution of film diffusion may also be taken into account more accurately, as has been done in an earlier paper [19].

II. EXPERIMENTAL METHODS OF INVESTIGATION

Two principal methods are used to study ion-exchange kinetics, *viz.* the shallow-bed technique (with a constant concentration in the outer solution) and the exchange between the solution and the ion exchanger in a limited volume of solvent (with a variable concentration of the solution). The first method has been most widely used, as considerable mathematical difficulties arise when dealing with the results obtained from experiments in a limited volume of solution. Some investigators consider that the main drawback to the further development and improvement in the "exchange in limited volume" method is the absence of a mathematical solution to certain basic equations which represent the exchange process under these conditions.

1. The Shallow-Bed Technique [4,10,13,20-23]

A diagram of the apparatus which was used in experiments on the kinetics of ion exchange in solutions [13,20,21,24] is shown in Fig. 3. 50 mg air-dried cation exchanger were charged into the cuvette, the base of which consisted of a fine mesh. A mesh was also fixed above the cation exchanger and the cuvette was placed in a stainless steel casing completely enclosed by a cover. The solution was passed through the cation exchanger at a rate of $\sim 8-10$ m s^{-1}. The measurements were carried out both on adsorption and desorption. When using the adsorption method the cation exchanger was first washed with a solution containing the same cation as in the cation exchanger. Then a solution containing the substituting cation (labelled with a radioactive isotope) was passed through over a known period of time, after which the cation exchanger was washed with distilled water and dried with acetone. The radioactivity of the cation exchanger after the known period of contact with the active solution was measured with an end-window counter. When using the desorption method the radioactive solution was first passed through the cation exchanger at a rate of ~ 0.2 cm s^{-1} until it was completely saturated with the radioactive isotope. Then the cation exchanger was washed over a known period of time at a high rate with a solution containing the substituting cation and the decrease in the activity of the cation exchanger measured as a function of the contact time with the non-active solution.

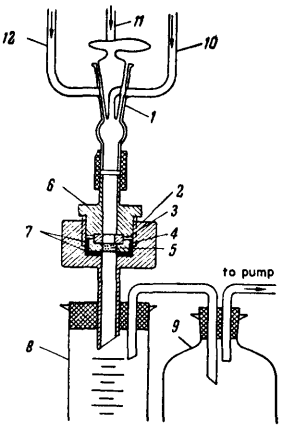

Fig. 3. Apparatus for measuring the diffusion coefficient in cation exchangers [24]: 1) four-way cock; 2) stainless steel casing; 3) washer for pressing nickel mesh against cell; 4) cation-exchanger cell; 5) cation-exchanger granules; 6) cover; 7) rubber washer; 8) measuring cylinder; 9) ballast vessel; 10), 11), and 12) connecting tubes.

2. The "Exchange in a Limited Volume of Solvent" Method

This was first used by Boyd and Soldano [12,25] to study self-diffusion and also by Dryden and Kay [26]. A weighed amount of ion exchanger was placed in a solution containing a radioactive isotope. After the tracer was uniformly distributed in the ion exchanger, the solution was removed and the ion exchanger washed with water and suspended in 150 ml distilled water in a vessel held in a thermostat. After reaching thermal equilibrium (after several hours) a volume (~ 50 ml) of the electrolyte at the same temperature and containing the same ion as the ion exchanger was added to the solution. The addition was made rapidly over 1–3 s. Then samples were removed from the solution and analysed until the activity of the sample remained constant. This method can also be used without radioactive tracers. For all its experimental simplicity, however, a fairly complex treatment of the results is needed to calculate the diffusion coefficients.

The diameter of the ion-exchanger particles must be known accurately to calculate the diffusion coefficient. In an earlier paper [20] the diameters of the ion-exchanger particles were measured in the swollen state under the microscope and the average of 400 measurements taken. The particles of an ion exchanger with an increased divinylbenzene content had a true spherical shape, but the particles of an ion exchanger with a low divinylbenzene content had an irregular shape, and the size of the particles was therefore determined from measurements in two directions.

III. SELF-DIFFUSION IN CATION EXCHANGERS

The self-diffusion coefficient of ions depends on a number of factors, primarily the degree of cross-linking [10,12,22,24], the nominal divinylbenzene (DVB) content, the temperature, and the ionic charge.

Boyd and Soldano [12] investigated the variation of the self-diffusion coefficients of Na^+, Zn^{2+}, and La^{3+} with cross-linking in an ion exchanger, using a wide range of DVB contents, 2–24% (Table 1).

Soldano [10] obtained similar results for the self-diffusion coefficients of the Na^+, Zn^{2+}, and Y^{3+} for a change in DVB content from 5 to 25%. For example, the self-diffusion coefficient of Y^{3+} decreases by more than two orders of magnitude with this change in DVB content.

It has been shown [24] that with a decrease in the DVB content of a cation exchanger from 12 to 7%, the self-diffusion coefficient of the Na^+ ion increases by a factor of 2.5 and that of Sr^{2+} by a factor of 8.

The variation of the self-diffusion coefficient with the charge on the ion has been studied [10,12,24,27-34]. The results of the first two papers [10,12] show good agreement and may be considered together (Table 2).

From the self-diffusion coefficients given above it may be seen that the self-diffusion coefficient varies approximately tenfold for a unit difference in the charge.

On investigating the Na^+, Ca^{2+}, and Sm^{3+} ions in Dowex-50 at 25° Holm [27] found that an increase of unity in the charge reduces the self-diffusion coefficient by a factor of ~ 4.

However, the self-diffusion coefficient is not determined solely by the charge on the ion but still depends on its nature. From other data [24] it follows that the self-diffusion coefficient of the Na^+ ion in a cation exchanger containing 7% DVB is eighteen times greater than the self-diffusion coefficient of the Sr^{2+} ion and in a cation exchanger containing 12% DVB it is sixty times greater.

In a comparison of the self-diffusion coefficients for ions having the same charge the following values of $\overline{D}$ (in $cm^2\ s^{-1}$) were obtained for the alkali metals [12] under almost identical conditions (DVB content 8.6%, temperature 0.3°): Na^+ 3.50×10^{-7}, K^+ 6.28×10^{-7}, Rb^+ 6.36×10^{-7}, and Cs^+ 6.61×10^{-7}; *i.e.* in the decrease in their rate of self-diffusion, $Cs^+ \geq Rb^+ > K^+ > Na^+$, the order of the alkali metal ions corresponds to the decrease in their radii.

The effect of temperature on the self-diffusion coefficients has been studied [10,12,35-40]. The values of $\overline{D}$ shown in Table 1 for two temperatures (0.3° and 25°) indicate an increase in the self-diffusion coefficient with a rise in temperature.

TABLE 1. Variation of the self-diffusion coefficient with the degree of cross-linking of an ion exchanger [12].

DVB, %	Diffusing ion	Diffusion coefficient, D, $cm^2\ s^{-1}$	
		0.3°	25°
4	Na^+	$6.66 \cdot 10^{-7}$	$1.41 \cdot 10^{-6}$
8.6		$3.50 \cdot 10^{-7}$	$9.44 \cdot 10^{-7}$
Dowex-50		$1.15 \cdot 10^{-7}$	$2.88 \cdot 10^{-7}$
16		$6.58 \cdot 10^{-8}$	$2.40 \cdot 10^{-7}$
24		$2.69 \cdot 10^{-8}$	$1.00 \cdot 10^{-7}$
2	Zn^{2+}	$2.95 \cdot 10^{-7}$	$7.37 \cdot 10^{-7}$
8		$2.06 \cdot 10^{-8}$	$6.30 \cdot 10^{-8}$
Dowex-50		$8.77 \cdot 10^{-9}$	$2.89 \cdot 10^{-8}$
16		$3.12 \cdot 10^{-9}$	$1.16 \cdot 10^{-8}$
24		$5.52 \cdot 10^{-10}$	$2.63 \cdot 10^{-9}$
2	La^{3+}	$5.18 \cdot 18^{-8}$	$1.30 \cdot 10^{-7}$
4		$2.96 \cdot 10^{-8}$	$6.85 \cdot 10^{-8}$
8		$3.01 \cdot 10^{-9}$	$9.20 \cdot 10^{-9}$
16		$1.53 \cdot 10^{-10}$	$5.10 \cdot 10^{-10}$

TABLE 2. Effect of ionic charge on the self-diffusion coefficient.

Diffusing ion	Self-diffusion coefficient, at 25°, D, $cm^2\ s^{-1}$	Degree of cross-linking in resin
Na^+	$2.76 \cdot 10^{-7}$	10% DVB. Ref. 10
Zn^{2+}	$2.89 \cdot 10^{-8}$	
Y^{3+}	$3.18 \cdot 10^{-9}$	
Na^+	$2.88 \cdot 10^{-7}$	Dowex-50. Ref. 12
Zn^{2+}	$2.89 \cdot 10^{-8}$	
Y^{3+}	$3.18 \cdot 10^{-9}$	
Th^{4+}	$2.15 \cdot 10^{-10}$	
Na^+	$1.00 \cdot 10^{-7}$	24% DVB. Ref. 10
Zn^{2+}	$2.63 \cdot 10^{-9}$	
Y^{3+}	$2.18 \cdot 10^{-10}$	

The study of the effect of cation-exchanger capacity on the self-diffusion coefficient is of great interest. Unfortunately, it is difficult to prepare ion-exchanger samples having a different capacity but a constant cross-linking which, as we have seen, greatly affects the rate of self-diffusion. Self-diffusion has been investigated for samples of cation exchangers prepared from the desulphonation of a sulphonated polystyrene cation exchanger by prolonged heating in water above 100°. [10] The investigations showed (Table 3) that the self-diffusion coefficients drop considerably with a decrease in capacity, but the activation energies increase. In order to find out how the cross-linking of an ion exchanger is altered on desulphonation, experiments on the sorption of water were carried out. These experiments led to the conclusion that at the first stages of desulphonation a rupture of the bonds takes place, and at the later stages it is compensated by the formation of new bonds. Thus, it may be assumed that samples desulphonated to a capacity below 4 mg-equiv. g^{-1} of dry resin have approximately the same cross-linking.

The ionic strength of the external electrolyte solution has a very interesting effect on the self-diffusion coefficient [12,41,46]. Measurements of the self-diffusion coefficient at 25° for the Na^+ ion in a cation exchanger containing 8.6% DVB [12] gave the values $\overline{D} = 9.44 \times 10^{-7}$ $cm^2\ s^{-1}$ at an electrolyte concentration of 0.22 *N* and $\overline{D} = 11.1 \times 10^{-7}$ $cm^2\ s^{-1}$ at a concentration of 1.0 *N*. On increasing the ionic

TABLE 3. Effect of cation-exchanger capacity on the self-diffusion coefficient and the activation energy [10].

Capacity, mg-equiv. per g dry resin in H form	Self-diffusion coefficient, $cm^2\ s^{-1}$		Activation energy, cal $mole^{-1}$
	0.3°	25°	
4.3	$1.23 \cdot 10^{-7}$	$3.32 \cdot 10^{-7}$	6600
3.2	$6.84 \cdot 10^{-8}$	$1.9 \cdot 10^{-7}$	6660
2.5	$2.24 \cdot 10^{-8}$	$6.98 \cdot 10^{-8}$	8180

strength of the solution from 0.26 M to 0.53 M the self-diffusion coefficient of Y^{3+} in Dowex-50 cation exchanger fell from 3.18×10^{-9} to 2.83×10^{-9} cm^2 s^{-1}. However, the experimental measurement of diffusion coefficients at low concentrations is very difficult. Boyd and Soldano [12] also considered the effect of the nature of the anion on the self-diffusion coefficient at a constant ionic strength in the solution. For the Ag^+ ion at a concentration of 0.22 N in the external solution, and with 16% and 25% cross-linking, $\overline{D} = 2.85 \times 10^{-7}$ cm^2 s^{-1} in $AgClO_4$ solution and in $AgNO_3$ solution $D = 2.62 \times 10^{-7}$ cm^2 s^{-1}, *i.e.* the nitrate ion reduces the self-diffusion coefficient somewhat. This effect was not observed for the La^{3+} ion. The authors explained the effect of the ionic strength of the external electrolyte solution as a relative contribution of two processes: (1) the compressing action of the external electrolyte, which, on increasing the concentration, will increase the density of the spherical ion-exchanger particles and decrease the rate of the process, and (2) the penetration of the diffusing anions from the external solution into the exchanger, which may cause a decrease in the activation energy and therefore an increase in the diffusion coefficient.

The quantitative interpretation of the diffusion processes of ions in an ion exchanger is usually based on Eyring's theory of absolute rates of reaction [47], according to which the diffusion coefficient is

$$D = e\lambda^2 \frac{kT}{h} e^{\frac{\Delta S^{\neq}}{R}} e^{-\frac{E}{RT}}, \qquad (16)$$

where D is the diffusion coefficient, λ the distance between two equilibrium positions, k Boltzmann's constant, h Planck's constant, $\Delta S^{\neq}$ the entropy of activation, and E the activation energy.

Eyring's equation connects the value of the diffusion coefficient with the activation energy and entropy of activation of the process, the greater the entropy of activation the higher the diffusion coefficient.

At first glance it would seem natural to take the value of λ [12] as the distance between the active groups, *i.e.* a value of the order of 10×10^{-8} cm. However, this is too high. It is impossible to determine λ without certain further assumptions. Assuming that the entropy of activation for the K^+, Rb^+, Cs^+, and Ag^+ ions is zero (or close to zero), it seems to be more accurate to take $\lambda = 1.5 \times 10^{-3}$ cm, *i.e.* the value found by Wang [48] for self-diffusion in water.

The activation energy of self-diffusion depends on a number of fundamental factors characteristic of the cation exchanger and the cation taking part in the exchange process, *viz.* the degree of cross-linking of the cation exchanger [10,12,23], the temperature [12], and the charges and dimensions of the cations [12,23,29,38]. The effect of these factors may be inferred from the data in Table 4.

For the alkali metal series an increase in the activation energy with a decrease in the dimensions of the ions is observed. In their decrease in activation energy the alkali metals fall into a series of the following type: $Na^+ > K^+ > Rb^+ > Cs^+$. In the main, the activation energy also rises with an increase in the ionic charge.

The temperature dependence of the activation energy may be shown taking the Na^+ and Zn^{2+} ions as examples [12]. For temperatures of 6°, 18.35°, and 36.9° the activation energy for the Na^+ ion in a cation exchanger containing 8.6% DVB falls, being 7100, 6280, and 4640 cal mole^{-1} respectively. For the Zn^{2+} ion the activation energy in a cation exchanger containing 16% DBV varied from 8580 (6.6°) to 8440 (19°) and 7800 (37.5°) cal mole^{-1}. Similar data on the change in activation energy with the change in the degree of cross-linking have been reported elsewhere [10]. For the Zn^{2+} ion the activation energy is 5200, 7700, 8500, and 10 000 cal mole^{-1} for DVB contents of 4, 10, 16, and 24% respectively.

TABLE 4. Variation of the activation energy of self-diffusion with the degree of cross-linking of the cation exchanger and the charge on the cation [12].

Ion	Cross-linking, % DVB	Activation energy, cal mole^{-1}	Ion	Cross-linking, % DVB	Activation energy, cal mole^{-1}
Na^+	8.6	6500	Ag^+	8.6	5895
	16	8400		16	6590
	24	8620		24	7200
Cs^+	8.6	4790	Sr^{2+}	4	5640
	24	5205		16	10 980
Zn^{2+}	8	7040	La^{3+}	4	5520
	16	8520		8	7310
	24	10 250		16	7870

Soldano [10] associates the activation energy of the exchange process with two principal factors: the work of creating a passage for the diffusing particles in the exchange medium (in the majority of ionic systems in an aqueous medium this work is relatively constant and is independent of the size of the cation) and the work against the electrostatic interaction, which depends on the dielectric permeability of the medium, the degree of association of the ions, and the distances between them. However, it is impossible to explain the great changes in diffusion coefficient with change in the ionic charge as being due only to activation energies, as they depend to a considerable extent on changes in the entropy of activation. With an increased degree of cross-linking of the cation exchanger the value of $\Delta S^{\neq}$ rises and it is also increased by the multicharged ions themselves which can act as auxiliary cross-linking agents and thereby increase the density and the complexity of the system.

The entropies of activation have been considered as functions of the contribution from two opposing processes [12]: (1) the disturbance in the medium caused by the diffusing ion (the positive contribution), and (2) the electrical interaction of water (the negative contribution). The authors assume that the first effect will predominate for large diffusing ions and slight association with the ionic group, and the second effect will predominate with an increase in the degree of hydration. Eqn. (16) shows that the diffusion coefficient also depends on the activation energy and the entropy of activation. The effect of these two quantities is so complex that it was found impossible to determine the relative contribution from each of them. Nevertheless, Soldano [10] concludes that the activation energies of self-diffusion processes are comparable with the activation energies observed for the majority of aqueous systems, in contrast to the higher activation energies for ionic diffusion in solids. It is of interest to compare the self-diffusion coefficients of corresponding ions in water and in a cation exchanger. It has been noted in many papers [10-12,25,27,32,44,50-52] that the mobility of counter-ions in an ion exchanger is considerably less than the mobility of the same ions in water, particularly for multivalent ions. Summarising the available data, we may say that the absolute values of the diffusion coefficients for singly-charged counter-ions in averagely cross-linked cation exchangers are 0.3 to 0.1 of their values in aqueous solutions; for doubly-charged ions these figures are 0.2 to 0.01, and for triply-charged ions they are 0.1 to 0.001. [44]

The self-diffusion coefficients and activation energies of water in ion exchangers in various forms have been determined and compared with the same quantities in pure water [11]. The self-diffusion coefficient of water in pure water at 25° was found to be 30.1×10^{-6} cm^2 s^{-1} [11] and $23.4 \times \times 10^{-6}$ cm^2 s^{-1};[49] in a cation exchanger in the H form containing 4% DVB it was 9.14×10^{-6} cm^2 s^{-1} (25°) and in a cation exchanger in the La^{3+} form it was 8.20×10^{-7} cm^2 $\times$ $\times$ s^{-1} (3.4°). The activation energy for pure water is 4410 cal mole^{-1} and for a cation exchanger in the H form it is 4600 and 5200 (4% and 8% DVB respectively). Thus, the self-diffusion coefficients of water in an ion exchanger decrease with an increase in the degree of cross-linking and are less than the self-diffusion coefficients in water. In addition, they depend on the ionic form of the cation exchanger. The activation energy of the process increases little with an increase in the degree of cross-linking of the cation exchanger. Similar results on the self-diffusion coefficient of water have been presented elsewhere [10].

IV. DIFFUSION OF MICROCOMPONENT IONS

The cationic form of an ion exchanger remains practically unaltered during the diffusion in it of ions at microconcentrations. This enables the diffusion coefficient to be considered constant and to be calculated comparatively easily.

The rate of diffusion of microcomponent ions depends mainly on the same factors as the rate of self-diffusion, *viz.* the degree of cross-linking of the cation exchanger [21,24,25], the charge on the diffusing ion [24,25,53], and the temperature during diffusion [4,25], and also on factors peculiar to the given type of exchange, such as the effect of the cationic form and composition of the cation exchanger [4,13,21,24,25,34] and the concentration of the macrocomponent ion in solution [4,21,24,53].

Boyd and Soldano [25] considered the diffusion of a number of microcomponent ions in sulphonated polystyrene cation exchangers cross-linked with 8.6% and 16% DVB. Using as an example the diffusion of Na^+ microcomponent ions in a substantially hydrogen form of a cation exchanger, and of Na^+ in the Cs form of the resin, they showed that the diffusion coefficient decreases with an increase in the degree of cross-linking, but the activation energy for diffusion of microcomponent ions increases. For example, for the diffusion of sodium in the H form of a cation exchanger containing 8.6% DVB, $D = 8.82 \times 10^{-7}$ cm^2 s^{-1} and $E_{act} = 5320$ cal mole^{-1}, and for a DVB content of 16% $D = 3.90 \times 10^{-7}$ cm^2 s^{-1}, $E_{act} = 6880$ cal mole^{-1}.

Fedoseeva [24] obtained similar results for the effect of DVB content on the rate of diffusion of microcomponent ions.

An approximately linear relationship was found [24] for the variation of the diffusion coefficients of Na^+ and Sr^{2+} microcomponent ions with the degree of cross-linking in cation exchangers containing 7, 10, and 12% DVB. With an increase from 7% to 12% in DVB content the diffusion coefficients of Na^+ and Sr^{2+} microcomponent ions were reduced by factors of 2.5 and 4.8 respectively. Table 5 gives data for the effect of cross-linking in a cation exchanger on the diffusion of microcomponent ions [21].

Boyd *et al.* [53] noted a retardation in the exchange process with an increase in the charge on the microcomponent ion. The diffusion coefficients for Na^+, UO_2^{2+}, and Ce^{3+} ions from HCl solutions are 3.7×10^{-6}, 3.6×10^{-7}, and 9.4×10^{-9} cm^2 s^{-1} respectively. The effect of temperature on the diffusion coefficients of microcomponent ions is probably similar to the effect on the self-diffusion coefficients, although fewer studies have been concerned with this problem. The diffusion of Na^+ microcomponent ions from KCl solution at 30° and 13.5° has been studied [4], diffusion coefficients of 3.5×10^{-6} and 1.6×10^{-6} cm^2 s^{-1} respectively being obtained. An increase in the diffusion coefficient with temperature rise has also been found for Na^+ microcomponent ions in the caesium, potassium, and zinc forms of a cation exchanger [25].

TABLE 5. Variation of the diffusion coefficient of a microcomponent ion with the cross-linking of a cation exchanger [12]. External solution 1.0 *N*.

Form of cation exchanger	Diffusing ion	DVB content, %	D, cm^2 × × s^{-1}
RH	Sr^{2+}	12	$6.25 \cdot 10^{-8}$
RH	Sr^{2+}	7	$2.81 \cdot 10^{-7}$
RNa	Sr^{2+}	12	$5.50 \cdot 10^{-8}$
RNa	Sr^{2+}	7	$2.30 \cdot 10^{-7}$

The effect of particle size of a cation exchanger on the rate of absorption of microcomponent ions was studied, taking the extraction of Na^+ ions from HCl solutions as an example [4]. It was shown that the diffusion coefficient is virtually independent of the particle size. The diffusion coefficients have been measured for Na^+ and Rb^+ microcomponent ions from 0.1 *N* HCl solutions on to cation-exchanger granules 0.26 and 0.48 mm in diameter. The diffusion coefficient of the Na^+ ion was found to be $3.2 \times \times 10^{-6}$ cm^2 s^{-1} for both grain sizes, and diffusion coefficients virtually independent of granulation were obtained for the Rb^+ ion.

The effect of the cationic form of an ion exchanger on the diffusion coefficient is peculiar to the exchange of microcomponent ions [25]. Boyd and Soldano established that the diffusion coefficient of the Na^+ microcomponent ion in an ion exchanger containing an alkali metal ion or a hydrogen ion is higher than in an ion exchanger in the pure sodium form. In hetero-ionic exchangers, *i.e.* those containing ions of two or more types, the diffusion coefficient of sodium may reach the value of the self-diffusion coefficient of the principal ion, when the fraction of the sodium ion becomes very low (< 5%). For example, in a predominantly potassium form (96.7% K^+, 16% DVB) $D_{Na^+} = = 3.63 \times 10^{-7}$ cm^2 s^{-1} at 25°, which is close to the value of $D_{K^+} = 3.74 \times 10^{-7}$ cm^2 s^{-1}. This is also observed for the Cs^+ ion in the sodium form of the cation exchanger. For 90% sodium at 16% DVB the activation energy for the Cs^+ ion was 8220 cal mole^{-1}, and the activation energy of the Na^+ ion in the pure sodium form was 8400 cal mole^{-1}, *i.e.* a value not much greater. In a study of the mutual effect of the contents of Zn^{2+} and Na^+ ions in a cation exchanger on their diffusion, an almost linear relationship of D_{Na^+} and $D_{Zn^{2+}}$ with its composition was noted.

It was also noted that the rate of diffusion of both ions becomes less as the cation exchanger becomes saturated with the Zn^{2+} ion. The diffusion coefficient of the microcomponent Na^+ ion in the zinc form of the exchanger is

8.56×10^{-8} cm^2 s^{-1} and that of Zn^{2+} in the sodium form is 2.21×10^{-8} cm^2 s^{-1}. From these results the qualitative conclusion was arrived at, that the more mobile cations are slowed down and the less mobile cations are accelerated. This is also confirmed by the fact that in homo-ionic salt forms of an ion exchanger $\overline{D}_{Na^+} : \overline{D}_{Zn^{2+}} = 20$ but for hetero-ionic forms the same ratio is ~ 8. In this study the rate of diffusion of the Na^+ ion in a predominantly lanthanum form of the cation exchanger was measured. Although the $\overline{D}_{Na^+} : \overline{D}_{La^{3+}}$ ratio in pure salt forms is about 500 the diffusion of Na^+ for a sodium content of less than 10% in the ion exchanger decreased by a factor of 6 compared with the diffusion coefficient in the pure sodium form. All these results again confirm the conclusion that in hetero-ionic salt forms of an ion exchanger the more mobile ions are retarded and the less mobile ions are accelerated.

The diffusion of Rb^+ and Na^+ ions in various salt forms of KU-2 cation-exchanger resin† has been studied[13,34]. Table 6 shows that the highest diffusion coefficient for Rb^+ is observed for the H form of the exchanger ($3.7 \times \times 10^{-6}$ cm^2 s^{-1}) and the lowest for the Ca form ($1.5 \times \times 10^{-6}$ cm^2 s^{-1}). Thus, these studies[13] show that a cationic form has a marked effect on the mobility of the cation being studied. From the diffusion coefficients of the microcomponent Rb^+ ion in various cationic forms of an ion exchanger, the following series of cationic forms can be constructed in decreasing order of diffusion coefficients: H > K ≥ Na > Ca. A similar sequence has been noted for the microcomponent Na^+ ion: H > K > Na.[4]

It has been shown[21] that the diffusion coefficient of a microcomponent ion in a cation exchanger containing doubly-charged ions is rather low compared with a cation exchanger containing singly-charged ions, although this effect is small. Similar relationships have been noted elsewhere[24], some of the data on the diffusion coefficients of microcomponent ions in a cation exchanger containing 10% DVB being given in Table 7.

From the data given above it may be concluded that both singly- and doubly-charged cations diffuse more rapidly in a cation exchanger containing singly-charged cations than in one containing doubly-charged cations. The effect of

TABLE 6. Effect of the form of KU-2 cation-exchange resin on the diffusion coefficient of ^{24}Na, ^{86}Rb, and ^{45}Ca microcomponent ions[13,34].

Form of cation exchanger	$10^6 D_{Na^+}$, cm^2 s^{-1} Ref. 13	$10^6 D_{Rb^+}$, cm^2 s^{-1} Ref. 13	$10^6 D_{Ca^{2+}}$, cm^2 s^{-1} Ref. 34
H	2.6	3.7	0.43
K	—	1.6 (25°)	—
K	—	2.1 (28°)	—
Na	2.2	1.45 (20°)	—
Na	—	2.0 (26°)	—
Ca	—	1.15	0.16

† KU-2 is a monofunctional, strongly acid cation-exchange resin with $-SO_3H$ active groups, prepared by treating a swollen styrene–divinylbenzene copolymer with chlorosulphonic acid, then saponifying the sulphonyl chloride (Ed. of Translation).

TABLE 7. Variation of the diffusion of microcomponent ions with the form of the cation exchanger[24].

Form of cation exchanger	Diffusing ion	D_0, cm^2 s^{-1}	Concentration of external solution, N
Rb	Rb^+	$2.64 \cdot 10^{-6}$	0.165
H		$1.46 \cdot 10^{-6}$	0.165
Na	Na^+	$1.80 \cdot 10^{-6}$	0.165
Ca		$1.45 \cdot 10^{-6}$	0.165
Ca	Ca^{2+}	$0.98 \cdot 10^{-7}$	0.25
Na		$1.20 \cdot 10^{-7}$	0.25
Sr	Sr^{2+}	$1.0 \cdot 10^{-7}$	0.25
Na		$1.39 \cdot 10^{-7}$	0.25

the form of a cation exchanger on the rate of diffusion of ions becomes greater the higher the degree of cross-linking of the cation exchanger and the higher the charge on the diffusing ion. For example[21], if Sr^{2+} ions diffuse in a cation exchanger in the hydrogen form, then the diffusion coefficient of these ions in a cation exchanger containing 12% DVB is 2.9 times greater than the self-diffusion coefficient, but in a cation exchanger containing 7% DVB it is only 1.6 times as high. In a study of diffusion in a cation exchanger containing 12% DVB [24] it was noted that if the self-diffusion coefficient of an ion is 1.4 times as high as the diffusion coefficient of the microcomponent Na^+ ion in the strontium form of the cation exchanger, then the self-diffusion coefficient of the Sr^{2+} ions is less than the diffusion coefficient of the microcomponent Sr^{2+} ion in the sodium form of the cation exchanger by a factor of 2.5.

It has been stated in the literature that the diffusion coefficient apparently depends on the concentration of the external electrolyte solution. However, during a study of the absorption of Na^+ ions from KCl solutions in relation to concentration, it was found[4] that on changing the macrocomponent ion concentration from 0.1 M to 0.2 M the diffusion coefficient of the Na^+ ion remained constant ($3.5 \times \times 10^{-6}$ cm^2 s^{-1}). The diffusion coefficients measured for the Sr^{2+} microcomponent ion into the sodium form of a cation exchanger from 0.25 N and 1.0 N NaCl solutions differed quite insignificantly (2.62×10^{-7} and 2.34×10^{-7} cm^2 s^{-1} respectively). Attention should also be paid to the fact that the values for diffusion coefficients of microcomponents of 0.165 N, 0.25 N, and 1.0 N are in good agreement with other results[21,24]: 2.91×10^{-7} cm^2 s^{-1} (0.25 N) and $2.80 \times \times 10^{-7}$ cm^2 s^{-1} (1.0 N).

V. KINETICS OF COMPLETE EXCHANGE

We have considered the simplest cases of ion exchange, *i.e.* the processes of self-diffusion and the diffusion of microcomponent ions. In these processes there are virtually no changes in the form of the cation exchanger, so that it is assumed that the processes take place with constant values for the diffusion coefficients. In the case of complete exchange, the ionic form of the cation exchanger alters, so that it is impossible to assume that the diffusion coefficient is constant, for the exchanging ions may have substantially differing mobilities. In addition, the swelling of a cation exchanger alters with a change in its form. To characterise the processes in complete exchange, the concept of the effective diffusion coefficient is introduced, *cf.* Eqn.(12).

It is evident that in most cases the rates of complete exchange correspond to the rates of diffusion of the cations whose concentrations are low, *i.e.* to the rates of diffusion of the microcomponent ions. Therefore, a comparison of the rate of complete exchange with the rate of exchange of the same ions present in microconcentrations is advisable.

Of the cases of complete exchange, those in which the hydrogen ion participates[13,20,55-57] are of special interest. In the papers cited the effects of the following factors on the rate of exchange were studied: the concentrations of the exchanging ions in solution, the degree of cross-linking and the particle sizes of the ion exchanger, and the temperature of the process; the activation energy was determined. A study has been carried out[56] of the complete exchange between sodium and hydrogen ions on two sulphonated polystyrene cation exchangers having different degrees of cross-linking (5 and 17% DVB). Reichenberg[56] established that in the exchange of the H^+ ion from a resin with Na^+ from solution, the rate of exchange at high Na^+ concentrations in solution ($> 1.0\ N$) does not depend on the concentration of this ion, and is inversely proportional to the square of the radius of the exchanger particles. At low ion concentrations in solution ($< 0.05\ N$) the rate was proportional to the concentration of Na^+ ions in solution and inversely proportional to the radius of the exchanger particle. Thus, at low concentrations, the exchange process was limited by diffusion through the film of solution adjacent to the ion-exchanger particle. In the same investigation a study was made of the effect of temperature and the degree of cross-linking of the cation exchanger on the effective diffusion coefficient for the process, which was limited by particle diffusion. For a cation exchanger containing 5% DVB and a particle diameter of 544 μm, $D = 7.3 \times 10^{-6}$ cm^2 s^{-1} at 25° and 1.7×10^{-5} cm^2 s^{-1} at 50°, for a cation exchanger containing 17% DVB and a particle diameter of 546 μm, $D = 1.1 \times 10^{-6}$ cm^2 s^{-1} (25°) and 2.4×10^{-6} cm^2 s^{-1} (50°), and for the same cation exchanger but with a particle size of 893 μm, $D = 1.2 \times 10^{-6}$ cm^2 s^{-1} (25°). Thus, with an increase in the degree of cross-linking of the ion exchanger and for complete exchange there is a decrease in the diffusion coefficient. With a rise in temperature the usual increase in the diffusion coefficient is observed; the activation energy for both cation exchangers was ~ 5.9 kcal mole^{-1}. The diffusion coefficient did not depend on the size of the cation-exchanger particles.

Similar results were obtained in another investigation[57]. It was shown that for complete exchange between alkali metal ions in solution and the hydrogen ion in a cation exchanger at an external solution concentration less than 1.0 *N* the effective diffusion coefficient is independent of the grain size of the ion exchanger and increases with temperature. It was established that for complete exchange the alkali metals can be arranged in the following order, according to the effective diffusion coefficient in the exchange with the hydrogen ion: $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$. The activation energy for the exchange of the H^+ ion with the Na^+ ion was estimated as ~ 5 kcal mole^{-1}.

A study of complete exchange has been made[13] in the replacement of the H^+ ion in a cation exchanger by the Na^+ ion from 0.1 *N* NaCl. Fig. 4 shows the kinetic curves for the diffusion of the microcomponent Na^+ ion from 0.1 *N* HCl into a cation exchanger in the hydrogen form at 18°.

For complete exchange the diffusion coefficient of the Na^+ ion is 5×10^{-6} cm^2 s^{-1} and for the exchange of the microcomponent Na^+ ion it is 2.6×10^{-6} cm^2 s^{-1}, *i.e.* twice as high, which is perfectly explicable, as the mobility of the H^+ ion is much higher than that of the Na^+ ion.

Complete exchange between H^+ and Na^+ ions, and between H^+ and Rb^+ ions, has been studied in other investigations[20,24]. Some of the results for complete exchange between H^+ and Na^+ ions are given in Fig. 5 and Table 8. The most rapid process is the exchange of H^+ ions from the cation exchanger with Na^+ ions from the solution, the slowest process being the diffusion of microcomponent Na^+ ions into the cation exchanger in the hydrogen form. Complete exchange between Na^+ and H^+ ions takes place with effective diffusion coefficients lying between these two limiting values.

The results obtained[20] confirm the theoretical conclusions that the effective diffusion coefficients have their highest values in exchange processes involving hydrogen ions at low H^+ ion contents in a cation exchanger. At these stages, apparently, the effective diffusion coefficients are close to the diffusion coefficient of the microcomponent H^+ ion in the sodium or rubidium forms of the cation exchanger.

The kinetics for the complete exchange of the singly-charged ions Li^+, Na^+, and K^+ with the H^+ ion in 1.0 *N*

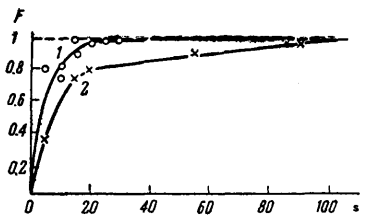

Fig. 4. Kinetic curves for complete exchange of hydrogen ions with sodium on KU-2 cation-exchange resin[13]: 1) 0.1 *N* NaCl + ^{24}NaCl (tracer) [? 2) 0.1 *N* HCl + + ^{24}NaCl [tracer], see text (Ed. of Translation)], cation exchanger in the hydrogen form.

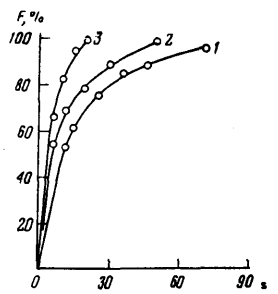

Fig. 5. Cation exchanger with a decreased DVB content[20]: 1) diffusion of Na^+ microcomponent ion in hydrogen form of cation exchanger; 2) exchange of sodium ions from the cation exchanger with hydrogen ions from solution; 3) exchange of hydrogen ions from the cation exchanger with sodium ions from solution.

TABLE 8. Effective diffusion coefficients in the exchange of sodium and hydrogen ions (sulphonated cation exchanger containing 7% DVB).[20]

System	Exchange period, s	Degree of exchange, F, %	$10^6 D_{eff}$, $cm^2 s^{-1}$
$RNa—H^+$	5	53.7	5.99
	10	69.0	5.50
	20	77.6	3.80
	30	88.2	4.18
	40	91.5	3.80
$RH—Na^+$	6	65.0	8.2
	10	81.0	10.2
	15	94.6	13.2
	20	97.0	13.0

TABLE 9. Effective diffusion coefficients for complete exchange between strontium and sodium ions[21].

System	Period of contact between solution and cation exchanger, s	Degree of exchange, F, %	D_{eff}, $cm^2 s^{-1}$	System	Period of contact between solution and cation exchanger, s	Degree of exchange, F, %	D_{eff}, $cm^2 s^{-1}$
$RSr—Na^+$	30	50.5	$9.6 \cdot 10^{-7}$	$RNa—Sr^{2+}$	10	51.0	$2.8 \cdot 10^{-6}$
	60	64.5	$9.1 \cdot 10^{-7}$		15	65.9	$3.3 \cdot 10^{-6}$
	80	73.0	$8.5 \cdot 10^{-7}$		25	77.2	$3.0 \cdot 10^{-6}$
	140	79.0	$7.3 \cdot 10^{-7}$		40	86.5	$2.94 \cdot 10^{-6}$
	180	80.0	$6.1 \cdot 10^{-7}$		60	90.5	$2.70 \cdot 10^{-6}$
	400	85.0	$2.8 \cdot 10^{-7}$		90	97.5	$2.85 \cdot 10^{-6}$
	520	91.0	$2.5 \cdot 10^{-7}$		120	99.3	—
	760	93.5	$2.3 \cdot 10^{-7}$		200	100	—

aqueous and aqueous alcoholic solutions have been studied[58]. The authors assumed also that in the initial stages of the exchange process the diffusion coefficients are constant, and therefore used for their calculations the equation for diffusion in a sphere involving a constant diffusion coefficient, *cf.* Eqn. (6). The diffusion coefficients thus found for aqueous solutions were, respectively. Li^+ 2.96×10^{-7}, Na^+ 4.55×10^{-7}, and K^+ 4.60×10^{-7} $cm^2 s^{-1}$. In addition, it was noted that in the exchange of the H^+ ion with the Li^+ ion the coefficient for diffusion from lithium sulphate solution is higher than from lithium chloride solution.

The complete exchange between singly-charged and doubly-charged ions has been studied[21,24]. In this case the kinetic characteristics are determined to a considerable extent by the difference in the properties of cation exchangers containing singly- and doubly-charged ions,

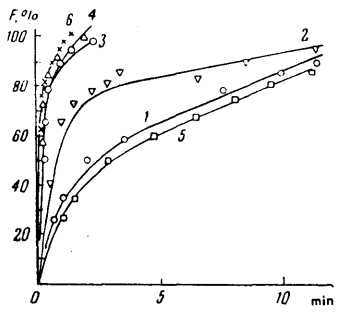

Fig. 6. Cation exchanger with a decreased DVB content. Exchange in 0.25 N solutions at 19–20°:[21] 1) diffusion of strontium microcomponent ions in the sodium form of cation exchanger; 2) exchange of strontium ions from the cation exchanger with sodium ions from solution; 3) exchange of sodium ions from the cation exchanger with strontium ions from solution; 4) diffusion of sodium microcomponent ions in the strontium form of cation exchanger; 5) self-diffusion of strontium ions; 6) self-diffusion of sodium ions.

particularly in swelling. The curves in Fig. 6 show that in the first stages the exchange of ions from a cation exchanger with the Na^+ ions from solution takes place much more rapidly than the diffusion of the microcomponent Sr^{2+} ion in the sodium form of the cation exchanger, but in later stages the rates of both processes approach each other. The calculated effective diffusion coefficients are shown in Table 9.

Thus, during the exchange process in the $RSr—Na^+$ system the effective diffusion coefficient falls and becomes an order of magnitude lower than the effective diffusion coefficient for complete exchange in the $RNa—Sr^{2+}$ system, whereas for exchange in the $RNa—Sr^{2+}$ system the effective diffusion coefficient is almost constant over the whole exchange process, being close to the diffusion coefficient of the microcomponent Na^+ ion in the strontium form of the cation exchanger. It should be noted that, at first, the exchange of Sr^{2+} ions in the cation exchanger with hydrogen ions takes place more rapidly than the exchange of Sr^{2+} ions with Na^+ ions, but in the later stages the rates of both processes become approximately equal. The initial difference in the rates of exchange is probably due to the higher mobility of the hydrogen ions in the cation exchanger, but at the later stages the rate of exchange is governed by the diffusion of the microcomponent strontium ion in the hydrogen or sodium forms of the cation exchanger.

VI. KINETIC FEATURES OF THE EXCHANGE OF LARGE ORGANIC IONS

The study of the kinetics of ion exchange processes during the sorption of large multicharged organic ions on a cation exchanger has a certain interest. Bruns *et al.*[59-66] showed that the rate of sorption of streptomycin ions on cation exchangers is determined by particle diffusion. It was established that the rate of exchange depends on a number of factors: the degree of cross-linking of the cation exchanger, the temperature, the concentration of ions in the solution, and the cationic form of the cation exchanger. It was found[59-61,63,64] that with an increase in the degree of cross-linking, diffusion in the cation exchanger is retarded and the amount of large ions absorbed becomes less than the total exchange capacity of the ion exchanger. Yakhontova *et al.* applied the concept of "pseudo-equilibrium" to this phenomenon. The establishment of "pseudo-equilibrium" was explained by the formation of a "streptomycin crust" on the surface of the grain of cation exchanger, it being assumed that the streptomycin form of the cation exchanger is only slightly permeable to streptomycin ions.

The observed retardation in sorption is most likely explained by the effect of a steric factor and the value of the ionic charge (the streptomycin ion is triply-charged).

A retardation in diffusion was also observed[67,68] when the sorption of the organic dyes Methylene Blue and Antipyridine Red and of other large organic ions was studied. The photomicrographs of sections obtained by these authors[67] show that intensive staining is observed only in the external layer of a granule, the central part remaining completely unstained.

The effect of the particle size of a cation exchanger on the rate of sorption was studied[59,60,64-73], it being shown that the greatest quantity of large organic ions is sorbed by a finely-dispersed cation exchanger, and a decrease in the amount of streptomycin absorbed is observed with an increase in the granule diameter. In particular[60], on using a cation exchanger in the hydrogen form containing 9% DVB and having grain sizes of 0.25–0.5 mm, the amount of streptomycin absorbed was half that absorbed on a cation exchanger having grain sizes of 0.03–0.06 mm. Furthermore, on crushing large grains after establishing a "pseudo-equilibrium" state on them, an additional absorption of streptomycin was observed. These phenomena may be explained by the fractional volume occupied by the "streptomycin crust" being considerably higher in the finer ion-exchanger particles.

The results concerning the effect of temperature on the sorption of streptomycin on a cation exchanger are interesting[59,61,63]. It was shown that a rise in temperature from 6° to 37° leads to an increase in the rate of diffusion by a factor of 2–4. The increase in temperature also leads to a displacement in the "pseudo-equilibrium", causing further sorption.

The form of the cation exchanger and the concentration of additional cations in solution have a substantial effect on the rate of sorption of large ions[59-66,68]. The authors[59-66] noted that the sodium form of the cation exchanger absorbs streptomycin better than the hydrogen form and that "pseudo-equilibrium" is shown most clearly by the hydrogen form of a cation exchanger (referring to a weakly acid cation exchanger). The exchange of streptomycin on the hydrogen form of a cation exchanger containing an average number of cross-links was investigated in solutions containing varying concentrations of sodium sulphate[60]. It was found that an increase in sodium ion concentration up to 0.3 N produced an increase in the sorption of streptomycin, but that a further increase to 1.0 N and 2.0 N led to a decrease in sorption. The time required for the completion of the exchange process fell considerably as the concentration was raised. Bruns *et al.* attributed this phenomenon to the mixed sodium–streptomycin form of the cation exchanger being more permeable to the streptomycin ion, *i.e.* the highly mobile, univalent sodium ion stimulates the diffusion of the tervalent streptomycin in the cation exchanger.

The diffusion coefficients of Methylene Blue ions in KU-2 sulphonated cation exchangers containing 2 and 6% DVB were studied for the initial periods of sorption[68], part of the hydrogen ions of the original exchangers being previously replaced by dye ions. It was established that in the sorption of dye ions on the exchanger containing 2% DVB, the diffusion coefficients of Methylene Blue ions in the cation-exchanger phase at 40° and 75° are approximately halved by an increase from 0 (the hydrogen form) to 0.8 (80% of the hydrogen ions replaced by dye ions) in the equivalent fraction of the dye ions in the initial ion exchangers. Precisely the same thing occurs for the sorption of the dye on the cation exchanger containing 6% DVB at 75°. On carrying out sorption at lower temperatures the diffusion of Methylene Blue ions in KU-2 containing 6% DVB decreased by from one to two orders of magnitude with the increase from 0 to 0.8 in the equivalent fraction of dye ions in the initial ion exchanger. In the latter case a large increase in the activation energy is observed and a "pseudo-equilibrium" state established.

Thus, the principal feature in the sorption of large organic ions should be considered, the decrease in the permeability of the cation exchanger towards the ion being absorbed during the exchange process (the "pseudo-equilibrium" state). This decrease in permeability is expressed as a decrease in the diffusion coefficients of large ions in the ion-exchanger phase and an increase in the activation energy with the conversion from one form to the other in the ion exchanger, the introduction of a univalent mobile ion in the exchange system leading to the liquidation of the "pseudo-equilibrium" state, an increase in the diffusion coefficient, and a decrease in the activation energy.

VII. THE RELATIONSHIP BETWEEN DIFFUSION AND ELECTRICAL CONDUCTIVITY IN ION EXCHANGERS

In conclusion we would like to dwell on the determination of the self-diffusion coefficients of ions in an ion exchanger by the direct measurement of electrical conductivity.

As is well known, the diffusion coefficient and mobility of the ions are connected by the relationship

$$D = \frac{R_T T B}{zF}, \qquad (17)$$

where T is the temperature in °K, B the mobility of the ion, R_T the gas constant, z the charge of the ion, and F Faraday's constant.

If the mobility of the ion is expressed in terms of the specific electrical conductivity and the transport number, the Nernst–Einstein relationship is written in the form

$$D = \frac{R_T}{zF} \times T \times \frac{1000 \kappa t}{aF}, \qquad (18)$$

where t is the transport number, κ the specific conductivity, and a the capacity of the ion exchanger calculated for 1 cm^3.

In electrolyte solutions placed in an electric field an external force proportional to the field strength acts on the ions, as well as two internal retarding forces, *viz.* an electrophoretic force, arising from the electric field which, in pulling the ion in one direction, draws off its ion atmosphere in the opposite direction, and a relaxation force arising from the loss of spherical symmetry in the ion atmosphere on moving.

Due to the presence of the retarding forces, the Nernst–Einstein relationship is satisfied only at infinite dilution in electrolyte solutions. For a cation exchanger it is to be expected that this relationship would be correct to a large extent, as a cation exchanger may be considered as a large immobile matrix to which anions and mobile cations are attached. The transport number of the cations in relation to such a matrix is close to unity.

It should be noted at once that according to the available experimental data the Nernst–Einstein relationship is satisfied for ion exchangers saturated with doubly- and multi-charged ions.

TABLE 10. Diffusion coefficients calculated from electrical conductivity data[72].

Capacity of cation exchanger, mg-equiv. × g^{-1}	Form of exchanger	Specific conductivity, Ω^{-1} cm^{-1}	Self-diffusion coefficient, $10^{-6}D$, cm^2 s^{-1} (calculated)
0.18	K	0.00063	0.022
4.5	H	0.092	18.7
4.5	Na	0.024	4.1
4.5	K	0.045	7.9
4.5	Sr	0.010	0.86

Many attempts to measure the electrical conductivity have been made on ion-exchange materials in the form of membranes or solid columns, but in a number of cases the preparation of materials in such a form is difficult, so that studies in which the electrical conductivity of ion exchangers in the form of granules has been determined[69-72] are of particular interest. For example, the specific conductivity of a KU-2 sulphonated cation exchanger having different capacities has been studied[72]. The measurements were carried out at 19° with chloride solutions. The basic idea behind the method is to find an electrolyte solution concentration whose electrical conductivity should equal the electrical conductivity of a cation exchanger particle in equilibrium with it. Using the values obtained for the electrical conductivity, the self-diffusion coefficients of the appropriate ions were calculated from Eqn. (18) (Table 10). In the calculations from the measured electrical conductivities a correction was made for the additional conductivity due to the Donnan effect. Here one should note the satisfactory agreement between the value of the self-diffusion coefficient for the Na^+ ion obtained by using a radioactive isotope on the same sample of cation exchanger ($D = 3.5 \times 10^{-6}$ cm^2 × × s^{-1}) and that calculated from the electrical conductivity data.

For K^+ too high a value of $\bar{D}$ seems to be obtained, while for Sr^{2+} a reasonable value is obtained. The low value of $\bar{D}$ for the K^+ ion in a low-capacity cation exchanger agrees with the decrease in self-diffusion coefficients observed on desulphonation[10]. The diffusion coefficients obtained for the hydrogen ion are anomalously high, but similar results were observed elsewhere[73]. It was found that in the exchange of the H^+ ion of an ion exchanger with Na^+ from solution, the effective diffusion coefficients are very high (up to 13 × × 10^{-6} cm^2 s^{-1}) and the hydrogen ion has an increased mobility in ion exchangers, as in aqueous solutions of electrolytes.

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ALPHA RADIOLYSIS OF AQUEOUS SOLUTIONS

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I. INTRODUCTION

Recent advances in nuclear chemistry, and in particular in the chemistry of the transuranium elements, have created a need for a better understanding of the effects of α-radiation on the physicochemical properties of a system. Furthermore, the high ionisation density of the α-radiation from radioactive elements offers a convenient simulation of the radiochemical processes occurring in solutions irradiated by fission residues. Hence the need for coordinating the experimental data relating to α-radiolysis is self-evident, particularly since the published results of different authors are often contradictory.

The decomposition of water under the influence of α-particles was first observed at the beginning of the present century, but no systematic studies were made until the late 1940's. The first experiments relied on radon as a source of α-radiation. The drawbacks of radon as an α-emitter are obvious: heterogeneous radiation, short half-life, and the inconvenience of working with a gaseous material. ^{210}Po is more convenient, being a practically pure α-emitter (one γ quantum per 10^5 α-disintegrations) with a half-life of 138 days. A further advantage of polonium is the very small mass of dissolved polonium needed to give high radiation intensities (1 curie of Po corresponds to 2.24×10^{-4} g). The disadvantage of polonium is the fact that it cannot be used as an internal α-source in weakly acid, neutral, and weakly alkaline solutions (pH 4–10) because of the extensive hydrolysis of its compounds. These solutions are studied with external polonium sources.

The first attempts at using dissolved polonium as a source of α-radiation, in 1948, proved unsuccessful. Bonet-Maury and Lefort[1,2] failed to detect hydrogen peroxide in 0.8 N H_2SO_4, in contrast to their experiments with radon[3,4]. Their conclusion that the polonium catalyses the decomposition of hydrogen peroxide was later confirmed[5,6]. On the other hand, Haissinsky and Anta[7,8], who studied the effect of α-radiation from dissolved polonium on solutions of bivalent iron and quadrivalent cerium, found that the radiochemical yields for cerium reduction and for iron oxidation were indistinguishable from those obtained with radon radiation[9,10] or with an external polonium source[11,12]. The French workers subsequently established[13–15] that the decomposition of hydrogen peroxide is caused by various impurities introduced into the solution during preparation of the polonium from RaD, and not by polonium ions. Radiochemical yields of hydrogen peroxide similar to those obtained with radon radiation were achieved by using polonium purified by various methods.

At the present time polonium is prepared by irradiating bismuth with neutrons ($^{209}Bi + n_0 \rightarrow {}^{210}Bi \xrightarrow{\beta} {}^{210}Po$). Ershova and Vladimirova[16] have described a method of separating the polonium from the bismuth which gives polonium pure enough to be used as an internal α-source. Polonium can also be used in external α-sources. The construction and method of use of external polonium sources are discussed in papers by Miller and Wilkinson[12], Senvar and Hart[17], and Hart and Teranday[18].

Besides Po and Rn, other radioactive elements (Pu, Am, Cm, Np), and accelerated helium nuclei and α-particles produced in various nuclear reactions, can be used as sources of α-particles in radiation studies.

II. RADIOLYSIS OF WATER AND AQUEOUS SULPHURIC ACID SOLUTIONS

1. Hydrogen Peroxide

Several workers have measured the radiochemical yield† of hydrogen peroxide in water and in 0.8 N sulphuric acid (Table 1).

† The radiochemical yield is defined as the number of molecules, atoms, ions, free radicals, etc., formed (or consumed) when the system absorbs 100 eV of ionising radiation. It is standard practice to write the appropriate formula in parentheses after the letter G (which denotes radiochemical yield).

TABLE 1. Radiochemical yield $G(H_2O_2)$.

Composition of solution	Source of radiation	$G(H_2O_2)$	Reference
Water	Rn	0.94	19
Water	Po (external)	1.28	17
Water + O_2*	Po (external)	1.33	17
Water + O_2	Rn	1.10	20
0.8 N H_2SO_4	Po (dissolved)	0.95	15
0.8 N H_2SO_4	Po (dissolved)	1.10	21
0.8 N H_2SO_4 + O_2	Po (dissolved)	1.15	15
0.8 N H_2SO_4 + O_2	Po (dissolved)	1.25	21
0.8 N H_2SO_4 + O_2	Po (dissolved)	1.20	16

* The oxygen concentration corresponds to saturation with air under normal conditions.

It is clear from Table 1 that $G(H_2O_2)$ in water and in 0.8 N sulphuric acid is close to unity. The large scatter of the $G(H_2O_2)$ values for the radiolysis of water is probably due to experimental error in the measurement of energy absorption when working with external sources of α-radiation. In air-free solutions $G(H_2O_2)$ is lower than in aerated solutions.

Lefort[5] studied the effect of oxygen at concentrations ranging from 3×10^{-5} M to 4×10^{-4} M, but could not detect any difference in the value of $G(H_2O_2)$. Trumbore and Hart[21] found an increase in the yield of hydrogen peroxide from 1.10 to 1.70 molecules per 100 eV on varying the concentration of dissolved oxygen from 0 to 0.1 M in 0.8 N sulphuric acid. They calculated the rate constant of the reaction $H + O_2 \rightarrow HO_2$, which they believe to be responsible for the increase in the yield of H_2O_2. $K(H + O_2) = 2.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

The influence of pH on the yield of hydrogen peroxide is examined in a number of papers. Bonet-Maury and Lefort[22] found that $G(H_2O_2)$ remains constant on changing the pH of water from 1 to 12. Vladimirova[23] observed a decrease in $G(H_2O_2)$ from 1.35 to 1.27 as the pH was varied from 7 to 2. Koulkes-Pujo[24] measured the yield of hydrogen peroxide over a wide range of pH: in neutral and acid media $G(H_2O_2) \simeq 1$, but in NaOH solutions and at pH 13–14 the yield is extremely small.

The influence of sulphuric acid concentration on the yield of hydrogen peroxide has also been investigated[23]. As the sulphuric acid concentration was varied from 0.4 M to 4.0 M, $G(H_2O_2)$ fell from 1.20 molecules per 100 eV to zero. The authors suggest that OH radicals from the tracks can take part in the reactions

$$HSO_4 + OH \rightarrow HSO_4 + OH,$$
$$H_2SO_4 + OH \rightarrow HSO_4 + H_2O,$$

when the concentration of sulphuric acid is increased. These reactions compete with the formation of hydrogen peroxide by recombination of the OH radicals. Good agreement with diffusion theory calculations for a cylindrical track was obtained. The rate constant for the reaction between hydrogen sulphate ions and OH radicals was calculated: $K(OH + HSO_4^-) = 0.7 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.

2. Gaseous Radiolysis Products

The yields of hydrogen and oxygen have been measured by several workers (see Table 2).

TABLE 2. Radiochemical yields of H_2 and O_2.

Composition of solution	Source of radiation	$G(H_2)$	$G(O_2)$	Reference
Water	Rn	1.8	0.42	19
Water	Po (external)	1.45	0.10	17
Water + O_2	Rn	1.70		20
0.8 *N* H_2SO_4	Rn	1.80	0.40	19
0.8 *N* H_2SO_4	Po (dissolved)	1.80	0.38	15
0.8 *N* H_2SO_4	Po (dissolved)	1.40	0.07	21
0.8 *N* H_2SO_4	Po (dissolved)	1.37	0.15	25
0.8 *N* H_2SO_4	Pu (dissolved)	1.60		26

TABLE 3.

Particle energy, MeV	LET*, eV Å^{-1}	$G(H_2)$	$G(H_2O_2)$	Reference
32	2.2	0.97—1.15	1.20	30,33,34
22	3.0	1.14		34
11	5.0		1.24	30
5.3	13.0	1.40	1.20	31
3.4	17.5	1.45	1.30	17
1.5	22.0	1.65		33

* LET = linear energy transfer.

The radiochemical yields for hydrogen and oxygen reported by different authors show a large scatter. The present writer believes that the measurement of oxygen yield presents a number of difficulties. The work of Hart[27] and Donaldson and Miller[28] has shown that the radical HO_2 is formed in the neighbourhood of the track, and decomposes to give oxygen ($HO_2 + H_2O_2 = OH + H_2O + O_2$). As hydrogen peroxide accumulates, a similar reaction can also take place in the bulk of the solution, producing additional oxygen. Hence, the oxygen yield will depend on the level of absorbed energy used in its measurement. The reasons for the scatter in the reported radiochemical yield of hydrogen are less obvious. The values $G(H_2)$ = 1.7–1.8 molecules per 100 eV are probably too high. According to Lefort[29], a hydrogen yield of 1.7 can only obtain in the presence of dissolved acceptors for OH radicals. This conclusion is at variance with Lefort's own results in Table 2, and confirms our view that $G(H_2)$ during α-radiolysis is close to 1.40 molecules per 100 eV.

The influence of sulphuric acid concentration on the yields of hydrogen and oxygen was studied by Vladimirova and Ershova[25], who found that $G(H_2)$ per 100 eV of energy absorbed by the water increases from 1.37 to 1.55 molecules per 100 eV when the concentration of H_2SO_4 is raised from 0.4 to 4.0 M. Schwarz and coworkers[30], using accelerated particles, also observed a higher $G(H_2)$ in sulphuric acid than in water.

3. Influence of Dose Rate, α-Particle Energy, and Amount of Energy Absorbed on the Yields of Hydrogen and Hydrogen Peroxide

Vladimirova and others[16,30] showed that $G(H_2O_2)$ keeps a constant value of 1.20 molecules per 100 eV when the concentration of dissolved polonium is varied from 0.1 to 12 mc ml^{-1}, corresponding to a change in dose rate from 1.9×10^{13} to 2.3×10^{15} eV ml^{-1} s^{-1}. When the dose exceeds 1.5×10^{20} eV ml^{-1}, $G(H_2O_2)$ gradually drops, and the amount of hydrogen peroxide tends towards a limiting concentration of the order of 0.01 M. For comparison, it may be noted that, according to Hochanadel[32], the steady-state concentration of hydrogen peroxide during γ-radiolysis in water is less than 10^{-6} M.

The radiochemical yield of hydrogen kept a constant value of 1.37 molecules per 100 eV when the dose rate was changed from 2×10^{13} to 2×10^{16} eV ml^{-1} s^{-1}, *i.e.* by three orders of magnitude. The $G(H_2)$ value remained constant for doses ranging from 5×10^{18} to 4×10^{20} eV ml^{-1}.

It is clear from the results of Table 3 that the radiochemical yield of hydrogen peroxide, $G(H_2O_2)$, is practically independent of the energy of the α-particles, whereas $G(H_2)$ increases as the energy of the particles decreases and as the linear energy transfer increases.

4. Influence of Dissolved Substances on the Yields of Hydrogen and Hydrogen Peroxide

Various authors have examined the influence of halide ions on $G(H_2O_2)$. Senvar and Hart[17] found that the radiochemical yield of H_2O_2 drops from 1.24 molecules per 100 eV to zero when the concentration of I^- is varied from 10^{-5} M to 0.1 M. The authors' calculations satisfactorily accounted for the experimental results in terms of diffusion theory. Burton and Kurien[35] also reported a decrease in $G(H_2O_2)$ with increase in concentration of acceptors (bromide and chloride ions). Anta[15] studied the effect of various additives on the yield of hydrogen peroxide, and found a decrease (from 1.15 to 0.19 molecules per 100 eV) upon changing the concentration of chloride ions from $2.6 \times \times 10^{-3}$ M to 5×10^{-2} M. Increasing the concentration of NO_3^- ions from 0.003 M to 0.4 M lowered $G(H_2O_2)$ from 1.15 to zero. The author ascribes reducing properties to the OH radical, and accordingly believes that the decrease in $G(H_2O_2)$ is due to the reaction

$$OH + NO_3^- \rightarrow NO_3^{\cdot} + HO_2^-.$$

Lefort and Cottin[20,36] showed that addition of such substances as KBr, KCl, KI, $KBrO_3$, KIO_3, HCOOH, KNO_3, $K_2Cr_2O_7$, $KMnO_4$, $Ce(SO_4)_2$, $Cr_2(SO_4)_3$, $FeSO_4$, and C_2H_5OH to 0.8 *N* sulphuric acid lower the yield of H_2O_2 very significantly, whereas additions of C_6H_6, NH_2NH_2, acrylonitrile, phosphite, and arsenite do not decrease $G(H_2O_2)$. In all the solutions investigated $G(H_2)$ remained constant at the level 1.7–1.8 molecules per 100 eV. Vladimirova[25,31] has examined the effect of various acceptors for OH radicals (glucose, Methylene Blue, and hydrogen) on the radiochemical yield of hydrogen peroxide and hydrogen. When the concentration of glucose was increased from 0.001 to 0.01 M, $G(H_2O_2)$ rose to 1.60 molecules per 100 eV, but fell to 1.09 molecules per 100 eV when the glucose concentration was increased still further. An increase in Methylene Blue concentration from 1×10^{-5} M to 7×10^{-5} M also increases $G(H_2O_2)$ (to 1.5 molecules per 100 eV). A similar increase in $G(H_2O_2)$ was observed on saturating the solution with hydrogen. The author explains these results in terms of Pucheault's assumption[37,38] of a second heterogeneous region adjacent to the tracks, in which the molecular products formed in the tracks (but unable to diffuse into the bulk of the solution) are thought to react with free radicals, *e.g.*

$$H_2O_2 + OH \rightarrow HO_2 + H_2O, \quad (a)$$

$$H_2 + OH \rightarrow H + H_2O, \quad (b)$$

$$H_2O_2 + H \rightarrow OH + H_2O. \quad (c)$$

Reactions (a), (b), and (c) have been called "intratrack reactions" in the foreign literature. The term seems lacking in felicity, and should be abandoned in favour of

TABLE 4. Measurements of the yield of OH, H, and HO_2 radicals.

System	$G(OH)$	$G(H)$	$G(HO_2)$	Reference
Formic acid	0.43	0.43		40
Iron sulphate	0.46	0.46		12
Iron sulphate + copper sulphate (Cu^{2+})		0.73	0.25	28
Cerium sulphate + + thallium sulphate Tl^+ concn.:				39
3×10^{-3} M	0.40	0.59	0.21	
7×10^{-3} M	0.54	0.59	0.08	
Iron sulphate	0.95	0.65		41
Cerium sulphate		0.60		42
Thallium sulphate (Tl^{3+})	0.40	0.58		43
Cerium sulphate + formic acid	0.50	0.37		44
Methylene Blue		0.70		31

"track reactions". We shall denote the region within which these reactions proceed as the track region, to distinguish them from the track itself, which is the site of the recombination reactions OH + OH and H + H. The reality of track reaction (b) is confirmed by the experimental demonstration of the influence of sulphuric acid concentration on $G(H_2)$ (see p. 214), and also by the experiments with additions of glucose[25] in which $G(H_2)$ rose from 1.37 to 1.75 molecules per 100 eV for a change in glucose concentration from 0.001 M to 0.01 M.

Conditions such that the acceptors will react with the radicals: (1) in the bulk of the solution, (2) in the track region, or (3) in the track, can be established by addition, in various concentrations, of acceptors for OH or for H radicals. Under condition (1) the yield of radiolysis products should remain unchanged; condition (2) should lead to higher initial yields of molecular products, since reactions (a), (b), and (c) will be suppressed; condition (3) should lower the initial yield of molecular products.

5. Yields of Free-Radical Radiolysis Products

The conventional indirect methods of measuring yields of free-radical products are satisfactory only in experiments with "light" radiation of low ionisation density, to which homogeneous kinetics can be applied. With heavy particles the track effects become very significant, and the yields of products become sensitive to the concentrations of dissolved materials: under these conditions an indirect method gives very approximate values of the radiochemical yields of free-radical products. This is clearly shown by the results for various systems given in Table 4.

III. RADIOLYSIS OF AQUEOUS SOLUTIONS OF INORGANIC AND ORGANIC COMPOUNDS

1. The Fe^{2+}–Fe^{3+} System

The results for the α-radiolysis of $\sim 10^{-3}$ M solutions of Fe^{2+} in the presence of air, given in Table 5, show considerable scatter in the $G(Fe^{3+})$ values. The presently accepted value is 5.1–5.2 molecules per 100 eV.

There is some disagreement as to the influence of Fe^{2+} concentration on $G(Fe^{3+})$: Lefort and Tarrago[39] and Miller and Wilkinson[12] found that a change in Fe^{2+} concentration

TABLE 5. Radiochemical yield for the oxidation of iron in 0.8 N H_2SO_4 by the α-radiation of dissolved polonium.

$G(Fe^{3+})$ molecules per 100 eV	Reference	$G(Fe^{3+})$ molecules per 100 eV	Reference
6.0	7	5.1	21,46
6.2	45	5.2	44
5.6	41	5.08	47
5.5	39		

from 2×10^{-4} M to 10^{-2} M had no effect on the yield of oxidised iron, whereas Trumbore and Hart[21] reported an increase from 5.0 to 5.38 molecules per 100 eV following a change in Fe^{2+} concentration from 2×10^{-4} M to $2.5 \times \times 10^{-2}$ M. According to Miller and Wilkinson[12], $G(Fe^{3+})$ is not affected by increasing the sulphuric acid concentration from 5×10^{-4} to 0.5 M.

The effect of dissolved oxygen concentration on $G(Fe^{3+})$ has been examined by several authors (Table 6). Trumbore and Hart[21] ascribe the increase in $G(Fe^{3+})$ to a higher yield of the HO_2 radical, which is formed when oxygen accepts H atoms in the tracks of the α-particles. This view is supported by the experiments of Donaldson and Miller[28], who were able to decrease $G(Fe^{3+})$ to 2.1 molecules per 100 eV by adding Cu^{2+} ions, which act as acceptors for H and HO_2 radicals, at a concentration of 0.01 M.

The oxidation of Fe^{2+} is frequently used for the chemical assay of external sources of radiation. With polonium sources, the measurement of energy absorbed is a rather complex problem. It requires a knowledge of the degree of collimation of the beam of α-particles, of the stopping power of the mica or other materials used to protect the active surface of the source, and lastly of the energy of the α-particles which penetrate into the solution. The results of work on the variation of $G(Fe^{3+})$ with α-energy, using external polonium sources, are summarised in Table 7. Starred values of $G(Fe^{3+})$ were obtained with accelerated helium ions.

It is evident from Table 7 that $G(Fe^{3+})$ increases with increase in α-particle energy and with decrease in linear energy transfer. The significant discrepancies in the yields obtained by different workers for α-particles of a given energy arise from the difficulty of calibrating external sources of α-radiation.

2. The Ce^{4+}–Ce^{3+} System

The radiolysis of sulphuric acid solutions of Ce^{4+} has been adequately investigated. Values of $G(Ce^{3+})$ for aerated solutions are set out in Table 8.

TABLE 6. Effect of oxygen concentration on $G(Fe^{3+})$ in 3×10^{-3} M solutions of Fe^{2+} in 0.8 N H_2SO_4.

O_2 concentration, M	$G(Fe^{3+})$	Reference	O_2 concentration, M	$G(Fe^{3+})$	Reference
0.0	3.47	12	$1.1 \cdot 10^{-3}$	5.49	21
0.0	3.65	41	$4.1 \cdot 10^{-3}$	7.6	21
0.0	3.53	47	0.1	8.5	21
0.0	3.57	21	0.4	9.8	21
$2.2 \cdot 10^{-4}$	5.1	21			

TABLE 7. Variation of $G(Fe^{3+})$ with energy of α-particles and helium ions and with linear energy transfer (LET).

Energy, MeV	LET, eV Å^{-1}	$G(Fe^{3+})$	Reference	Energy, MeV	LET, eV Å^{-1}	$G(Fe^{3+})$	Reference
32	2.2	8.1 *	34,51	3.5	17.5	5.94	48,49
22	3.0	7.0 *	34	3.0	18.0	5.70	48,49
11	5.0	6.5 *	34	3.0	18.0	4.16	50
4.7	15.0	5.9	12	1.5	20.0	4.19	50
4.5	15.0	4.79	50	1.5	20.0	4.15	49
3.5	17.5	4.37	50	1.5	20.0	4.20	45
3.5	17.5	4.70	52	1.5	20.0	4.20	53

* These values were obtained with helium ions.

TABLE 8. Radiochemical yields of Ce^{3+} in solutions of Ce^{4+} salts in 0.8 N H_2SO_4.

Radiation source	$G(Ce^{3+})$	Reference
Rn	3.2	9
Po (dissolved)	3.3	54
Po (dissolved)	3.2	8
Po (dissolved)	3.2	42
Po (dissolved)	3.05	44
Po (external, $E\alpha$ = 3.4 MeV)	2.88	55

The agreement between the tabulated values is satisfactory. However, if the yields of α-radiolysis products are inserted into the equation giving $G(Ce^{3+})$ for γ-radiolysis a value of 2.5–2.7 ions per 100 eV is obtained. This is much lower than the experimental values. The failure of the accepted reduction scheme for cerium to explain the α-radiolysis results was also pointed out by Anta [15]. The constancy of the Ce^{3+} yield with changes in Ce^{4+} concentration between 10^{-5} M and 10^{-3} M, reported by Weiss and Miller [55], whether or not oxygen is present in solution, adds to the difficulty of interpreting the reduction mechanism of cerium.

The reduction of cerium is known to be very sensitive to the presence of dissolved compounds. Lefort and Tarrago [39] and Weiss and Miller [55] have shown that the yield of Ce^{3+} is slightly increased by Tl^+ ions added to the solution. Anta and Margu [56] found that an increase in nitric acid concentration from 2×10^{-2} M to 3 M raises $G(Ce^{3+})$ from 3 to 10 ions per 100 eV.

3. Aqueous Solutions of Some Other Inorganic Substances

Nitrate–nitrite system. A qualitative study of this system was made by Lefort [5] and Haissinsky and Lefort [57], who showed that the oxidation of nitrite to nitrate proceeds faster than the reverse reduction process. Anta [15], working with 0.8 N sulphuric acid solutions containing nitrate, found that $G(NO_2^-)$ is only 0.005 ions per 100 eV at a concentration of nitrate of 0.4 M. Kabakchi and coworkers [58,59] observed the formation of nitrite in yields ranging from 0.1 to 4 ions per 100 eV in aqueous solutions of nitrate (0.01 M to 6 M) subjected to α-radiation from ^{239}Pu. These large yields of nitrite may be attributed to the Griess reagent which was added to the solutions and stabilised the nitrite ions by combining with them.

$I^- - I_2$ system. Lefort [60] and Senvar and Hart [17] observed the formation of free iodine in their work on the radiolysis of KI solutions in 0.8 N sulphuric acid. The latter workers showed that the combined yield of iodine and hydrogen peroxide remains constant (1.30 molecules per 100 eV) over the whole range of KI concentration used in the investigation.

Phosphate–phosphite system. Cottin [61] studied α-radiolysis in this system, and observed phosphite oxidation with a yield depending on the concentration of phosphite in solution. Thus, PO_4^{3-} yields of 0.26 molecules per 100 eV and 1.01 molecules per 100 eV were obtained for HPO_3^{2-} concentrations of 2×10^{-4} M and 5×10^{-3} M respectively. Oxidation proceeds according to the reaction $HPO_3^{2-} + 2OH \rightarrow PO_4^{3-} + H_2O$.

Arsenite–arsenate system. Lefort and Haissinsky [62,63] found that arsenite is quantitatively oxidised to arsenate by the reaction $AsO_3^{3-} + 2OH \rightarrow AsO_4^{3-} + H_2O$.

$V^{4+} - V^{5+}$ system. Pucheault and Ferradini [37,64] proved that an equilibrium between the oxidised and the reduced form of vanadium is established in solution during α-radiolysis.

$U^{6+} - U^{4+}$ system. Zalkind and Veselovskii [65] examined the effect of α-radiation from radon on solutions of uranyl sulphate by an electrochemical procedure, and observed a non-equilibrium amount of U^{5+} formed by the reduction of uranyl ion by H radicals. U^{5+} is readily oxidised by OH radicals and by hydrogen peroxide: for this reason, no hydrogen peroxide or peroxidic compounds of uranium are found in solution at high concentrations of dissolved uranyl sulphate (1–1.5 M).

Haissinsky [66] studied the action of α-radiation from Po on U^{4+} solutions, and found that the oxidation yield depends on the initial concentration of U^{4+}. $G(U^{6+})$ = 3.9 molecules per 100 eV for a 3×10^{-3} M concentration of U^{4+}; $G(U^{6+})$ = = 13.7 for a 9×10^{-3} M concentration of U^{4+}.

4. Aqueous Solutions of Organic Compounds

Lefort and Haissinsky [68] observed, in their study of the radiolysis of aqueous hydrazine solutions (Table 9), that the yields of hydrolysis products depend on the acidity of the solution and on the hydrazine concentration, whilst the yield of hydrazine decomposition is independent of acidity (0.6 and 1.0 molecules per 100 eV for 10^{-4} M and 10^{-3} M concentrations respectively). They suggest the following scheme for the radiolysis of hydrazine:

$$N_2H_4 + 2H_2O_2 = N_2 + 4H_2O, \quad 2N_2H_4 + 2OH = N_2 + 2NH_3 + 2H_2O.$$

Hart [40] studied the α-radiolysis of aqueous solutions of formic acid in order to characterise the relative yields of free-radical and molecular radiolysis products. In a 10^{-3} M solution, CO_2 and H_2 were obtained in yields of 0.43 and 1.57 molecules per 100 eV respectively. Assuming that the radiochemical process is $HCOOH + OH + H + O_2 = H_2O + CO_2 + H_2O_2$, Hart calculated that the α-radiolysis yields 12% of free-radical products and 88% of molecular products.

Data on the α-radiolysis of aqueous solutions of glycine [67], obtained with an external polonium source (E = 4 MeV), are presented in Table 10. The concentration of H_2O_2 was monitored over a wide range of doses, and found to reach

TABLE 9. Radiochemical yield (molecules per 100 eV) of the radiolysis products of hydrazine.

N_2H_4 concn., M	10^{-4}	10^{-3}	10^{-4}	10^{-3}
	neutral solution pH 8		acid solution 0.1 N H_2SO_4	
N_2	0.55	0.7	0.35	0.55
NH_3	0.1	0.6	0.55	0.9
H_2O_2	—	—	0.8	0.4
H_2	1.6	1.7	1.65	1.65
O_2	0.25	0.2	0.2	0.2

TABLE 10. Yield of radiolysis products of a 1 M aqueous solution of glycine.

Radiolysis products	G, molecules per 100 eV	
	deaerated	in presence of air
NH_3	1.67	1.80
CH_3NH_2	0.24	
HCOCOOH	1.1>0.64	1.23>0.84
HCHO	0.42	0.57
CH_3COOH	0.16	
H_2O_2	>0.6	≃0.8

a steady-state level of about 1.5×10^{-3} M at doses of the order of 2×10^{20} eV ml^{-1}.

Vladimirova observed[31,69], in her study of the α-radiolysis of aqueous Methylene Blue solutions, that the yield of bleached dye varies exponentially with energy absorbed. Depending on the experimental conditions, the decolorisation can proceed reversibly or irreversibly. During irreversible bleaching of Methylene Blue in 0.8 N sulphuric acid solution, the variation of the radiochemical yield with dye concentration shows three distinct regions. The author points out that the OH radicals, which are responsible for the irreversible bleaching, can be accepted in three different regions: the bulk of the solution, the track region, and the track. Complete acceptance of the OH radicals in the bulk of the solution occurs at a Methylene Blue concentration of 5×10^{-5} M. Vladimirova suggests that the irreversible bleaching of Methylene Blue could be used in the dosimetry of dissolved polonium.

Alexander and Rosen[70,71] irradiated solutions of proteins and tryptophan, and found that the molecular products of α-radiolysis are more reactive than the radical products of γ-radiolysis. They suggest that the action of α-particles produces hydrogen peroxide in an active form (possibly an isomeric form) of lifetime 10^{-5} s and oxidising power similar to that of ozone. This is apparently the reason for the more drastic biological effects of α- than of γ-radiation.

5. Solutions of Compounds of the Transuranium Elements

A whole review article could be written on the α-radiolysis of solutions of the transuranium elements. Therefore we shall only briefly consider the main published data.

The use of α-radiation from the transuranium elements ^{239}Pu, ^{237}Np, and ^{241}Am for studying radiation processes in water or other media is complicated by the large concentration of these elements (10^{-3}–10^{-2} M) needed to produce even comparatively modest dose rates in the solution ($\sim 10^{15}$ eV ml^{-1} s^{-1}). Thus the radiation effects in the medium are masked by chemical reactions between the emitters themselves and the radiolysis products of water. The only exception is ^{242}Cm, which has a half-life of 167 days, *i.e.* close to that of polonium. The only reported use of curium as a source of radiation is a private communication from Miller on the value of $G(H_2O_2)$ in dilute sulphuric acid. Anta showed[15] that this agrees closely with the $G(H_2O_2)$ values given by polonium and radon radiation, which is not surprising, since the energy of α-particles from curium (and from the other transuranium elements) is not very different from the energy of the particles from polonium or radon.

Radiation processes in solutions of compounds of the transuranium elements are usually investigated by observing changes in the valence state of these elements brought about by their own α-radiation (self-reduction) or by radiation from polonium, which offers higher dose rates. From the results, the yields of molecular and free-radical radiolysis products in the given medium can be calculated. The values thus obtained (Table 11) agree satisfactorily with the radiochemical yields observed in experiments with polonium and radon radiation, with the exception of the calculated yield of H_2O_2 in 0.2 M $HClO_4$: according to Anta[15], $G(H_2O_2)$ in 0.4 M $HClO_4$ should be 1.35 molecules per 100 eV.

Plutonium salt solutions. The most extensive study of the α-radiolysis of various solutions of plutonium salts (Pu^{6+}) was reported by Pages[26,73,74] and by Artyukhin[75,76]. It was shown that Pu^{6+} is reduced to Pu^{3+} in 0.1 M perchloric acid, and to Pu^{4+} in 0.1–0.4 M sulphuric acid. In either solution the yield of Pu^{6+} reduction is 3.2 equiv. per 100 eV. In a 1.5 M sulphuric acid solution the reduction yield drops to 2.4. Pages assumes that the reduction of Pu^{6+} involves mainly hydrogen peroxide: $Pu^{6+} + H_2O_2 \rightarrow Pu^{4+} + O_2 + 2H^+$. By using polonium radiation, Pages demonstrated that the reduction of plutonium varies with dose rate. At the highest dose rates the reaction shows an induction period during which no reduction occurs. This is explained by the very fast accumulation of hydrogen peroxide, which fails to react with the plutonium ions.

TABLE 11. Yield of radiolysis products in solutions containing Pu and Am.

Solution	Radiation source	$G(H_2O_2)$	$G(H_2)$	$G(H)$	Reference
H_2SO_4 0.1 – 0.4 M	^{239}Pu	1.35 calc.	1.60 expt.		26
H_2SO_4 0.1 M	^{241}Am	1.18 expt. 1.16 calc.		1.86 calc.	72
H_2SO_4 1.0 M	^{241}Am	0.69 expt. 0.54 calc.		1.87 calc.	72
$HClO_4$ 1.0 M	^{239}Pu	1.35 calc.	1.60 expt.		26
$HClO_4$ 0.2 M	^{241}Am	0.78 calc.		1.73 calc.	72

TABLE 12. Yields for the reduction of Am in acid solutions.

H_2SO_4, M	$-G(AmO_2^{2+})$	$HClO_4$, M	$-G(AmO_2^{2+})$	HNO_3, M	$-G(AmO_2^{2+})$
0.1	4.18	0.2	4.18	0.5	7.1
1.0	2.95	2.0	3.31	3.0	8.9
2.0	2.59	4.0	3.31	6.0	9.0
4.0	2.09	6.0	3.52	9.0	10.6
6.0	1.86	9.0	2.9	14.3	6.0
10.0	2.28	12.0	0.0		

In 0.1–0.5 M solutions of nitric acid Artyukhin and Pages found no reduction of plutonium over a very long period, but after 25–50 days the reduction became very fast. The reduction of plutonium is insensitive to the acidity of the medium between the pH limits 2–5. The reduction yield is markedly affected by the concentration of nitrate ions[75]: as the NO_3^- concentration is increased from 0.1 *N* to 5.0 *N* (at pH 3), the reduction yield rises from 4 to 6.5 equiv. per 100 eV. The authors consider that reduction of Pu^{6+} in nitrate solutions involves hydrogen peroxide and nitrous acid:

$$2PuO_2^{2+} + H_2O_2 \rightleftarrows 2PuO_2^+ + 2H^+ + 2O\,,$$

$$2PuO_2^{2+} + HNO_2 + H_2O \rightleftarrows 2PuO_2^+ + NO_3^- + 3H^+\,.$$

Artyukhin explains the retardation of the reduction of Pu^{6+} in more concentrated nitric acid by an increase in the rate of reaction of PuO_2^+ with NO_3^-.

Americium salt solutions. The valence changes of americium caused by its own α-radiation are discussed in detail in the papers by Yakovlev and Kosyakov[77,78] and by Zaitsev *et al.*[72] When mixed solutions of Am^{6+} and Am^{5+} in sulphuric or perchloric acid are reduced, the Am^{5+} remains unaffected until the whole of the Am^{6+} has been reduced. In nitric acid, reduction of Am^{5+} is very slow. Reduction yields for Am^{6+} in different acid solutions are set out in Table 12.

The following scheme for the reduction of Am^{6+} is proposed:

$$AmO_2^{2+} + HO_2 \rightarrow AmO_2^+ + O_2 + H^+\,,$$

$$AmO_2^{2+} + H_2O_2 \rightarrow AmO_2^+ + HO_2 + H^+\,.$$

The decrease in reduction yield at higher sulphuric acid concentrations is ascribed to the increasing effect of the reaction $HSO_4^- + OH \rightarrow HSO_4 + OH^-$, which competes for OH radicals and therefore lowers the yield of hydrogen peroxide. The decrease in reduction yield of Am^{6+} in concentrated perchloric acid solutions is explained by the authors in terms of the inhibiting effect of Cl_2 and ClO_2, which are produced by decomposition of the acid itself. The increase in reduction yield in nitric acid solutions is said to be due to secondary products formed by the action of free radicals upon nitric acid.

Neptunium salt solutions. The self-reduction of neptunium (Np^{6+}) in perchloric acid solutions was studied by Zielen *et al.*[79] At neptunium concentrations of the order of 0.2 M the reduction yield is 6.4 molecules per 100 eV, and does not vary with perchloric acid concentration within the limits investigated (0.5–1.7 M). This high reduction yield is attributed to the high concentration of neptunium in solution: in the investigations discussed above the concentration of plutonium and americium was never higher than 10^{-2} M.

IV. MECHANISM OF α-RADIOLYSIS

Available experimental data on the α-radiolysis of aqueous solutions can be satisfactorily described by the concepts of the free-radical theory of radiolysis, leading to a fairly accurate mechanism for the process.

The high ionisation density associated with α-particles gives rise to a considerable local concentration of free radicals along the tracks: $[OH] \simeq 0.1$ M; $[H] \simeq 0.01$ M. The recombination of radicals in the tracks (by the reactions OH + OH and H + H) leads to the formation of molecular products. Whereas the mechanism of formation of hydrogen peroxide is beyond doubt, various statements regarding the formation of molecular hydrogen appear to the present writer to be based on contradictory experimental data. The apparent constancy of $G(H_2)$ in 0.8 *N* sulphuric acid containing various solutes led Haissinsky to conclude, for example[80], that hydrogen is formed directly by the reaction $H_2O^- \rightarrow H_2 + O^-$. However, the results of Donaldson and Miller[28] on the acceptance of H atoms by Cu^{2+} ions, and Vladimirova's observations[25,31] that H atoms are accepted by NO_3^- ions and by Methylene Blue, force the conclusion that the hydrogen is produced by recombination.

Hart estimated that about 88% of the radicals during α-radiolysis recombine to give molecular products, the proportion of free radicals in the product being only 12%.

Pucheault[37,38] made a significant contribution to a deeper understanding of the mechanism of α-radiolysis by his detailed study of the track region and track reactions.

In what follows, we shall attempt to present the mechanism of α-radiolysis of water on the basis of the experimental results reported for systems containing 0.8 *N* sulphuric acid.

Yields‡ of molecular products:

$$G^{O_2}(H_2O_2) = 1.20,\ G(H_2O_2) = 1.0,\ G_{H_2O_2} = 1.75,\ G(H_2) = 1.40\,,$$

$$G^{Fe^{2+}}(H_2) = 1.60,\ G_{H_2} = 1.80.$$

Yields of track reactions:

$$G_{(a)} = G_{HO_2} = G(HO_2) = 0.2,$$

$$G_{(b)} = G_{H_2} = G(H_2) = 0.4,$$

$$G_{(c)} = G_{H_2O_2} = G_{(a)} - G(H_2O_2) = 0.35.$$

The present writer believes that the scheme should include a fourth track reaction (*d*), which provides an alternative path for the formation of hydrogen peroxide in solution: $2H + O_2 = H_2O_2$

$$G_{(d)} = 2\,[G^{O_2}(H_2O_2) - G(H_2O_2)] = 0.4\,.$$

Yield of H and OH radicals. In the absence of dissolved oxygen it seems preferable to determine the yield of OH radicals starting from data on the oxidation of Fe^{2+}. The yield of Fe^{3+} in a vacuum is 3.6 molecules per 100 eV. The yield of hydrogen in a solution containing Fe^{2+} ions is higher than in 0.8 *N* sulphuric acid by 0.2. Since it is known that an equivalent amount of hydrogen is evolved

‡ The superscript after the symbol *G* refers to the compound present in solution. Initial yields of the radiolysis products of water are designated by the symbol *G* with the appropriate subscript, *e.g.* $G_{H_2O_2}$.

when iron is oxidised by H radicals in the absence of oxygen, we may assume that $G(H)$, the yield of H radicals reacting with Fe^{2+}, is 0.2 molecule per 100 eV.

$G(Fe^{3+})$ in a vacuum is described by the equation

$$G(Fe^{3+}) = 2G(H_2O_2) + G(OH) + 3G(HO_2) + G(H).$$

Hence $G(OH)$ = 3.6 - 2.0 - 0.6 - 0.2 = 0.8 molecule per 100 eV. To find $G(H)$ in 0.8 N H_2SO_4, we use the material balance equation

$$-G(H_2O) = 2G(H_2O_2) + G(OH) + 3G(HO_2) = 2G(H_2) + G(H).$$

Hence $G(H)$ = 2.0 + 0.8 + 0.6 - 2.8 = 0.6 molecule per 100 eV.

In the presence of dissolved oxygen the yields of OH and H can be calculated from the two equations

$$G^{O_2}(Fe^{3+}) = 2G^{O_2}(H_2O_2) + G^{O_2}(OH) + 3G(HO_2) + 3G^{O_2}(H),$$
$$-G^{O_2}(H_2O) = 2G^{O_2}(H_2O_2) + G^{O_2}(OH) + 3G(HO_2) = 2G(H_2) + G^{O_2}(H) + G(d).$$

Inserting known numerical values, we find

$$G^{O_2}(OH) = 0.7, \quad G^{O_2}(H) = 0.5 \text{ molecule per 100 eV.}$$

Yield of water decomposition. The observed yield of water decomposition in the presence and in the absence of dissolved oxygen can be deduced from the material balance equation:

$$-G(H_2O) = 3.4 \text{ molecules per 100 eV}, \quad -G^{O_2}(H_2O) = 3.7.$$

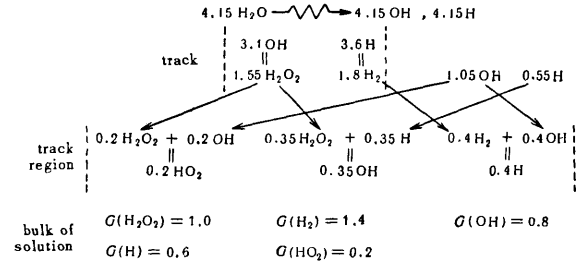
To calculate the initial yield of water decomposition, allowance must be made for the track reactions:

$$-G_{H_2O} = -G(H_2O) + G_{(b)} + G_{(c)}.$$

Inserting the appropriate values for the yields of the track reactions and of the water decomposition we find

$$-G_{H_2O} = 4.15 \text{ molecules per 100 eV}, \quad -G^{O_2}_{H_2O} = 4.45.$$

These results enable us to put forward the following scheme for the mechanism of α-radiolysis:



The scheme shows the further transformations of free-radical and molecular products after their formation from ionised water molecules. Thus, the initial yield for the decomposition of water during α-radiolysis is 4.45 molecules per 100 eV, *i.e.* the same as for γ-radiolysis. It is significantly higher than the previously accepted value of 3.6 molecules per 100 eV, which characterises the observed yield. The observed yield for the decomposition of water, as well as the observed yields of free-radical and of molecular products, may vary with the concentration of various solutes, but the initial yield for the decomposition of water should remain constant.

From these results we may conclude that the initial yield for the decomposition of water should be independent of the type of radiation used. The only difference in the mode of action of the various types of radiation concerns the magnitude of the linear energy transfer: with radiations having a small linear energy transfer all the decomposed water molecules can be easily accounted for in terms of processes occurring in the solution, whereas with radiations with a large linear energy transfer the initial radiolysis products are partly decomposed in the track region.

In his development of the hypothesis of track reactions and the track region Pucheault[81] attempted to demonstrate the likelihood of reactions (a), (b), and (c), and to estimate the relative sizes of their regions. The removal of radiolysis products from the tracks, and their collision probabilities, depend on their diffusion coefficients D (other conditions being equal). Introducing the notation

$$\frac{1}{\beta_a} = \frac{D_{H_2O_2}}{D_{OH}}, \quad \frac{1}{\beta_b} = \frac{D_{H_2}}{D_{OH}}, \quad \frac{1}{\beta_c} = \frac{D_{H_2O_2}}{D_H},$$

and using the relation $D = \sqrt{1/M}$, we obtain

$$\beta_a = \sqrt{\frac{34}{17}} = 1.41, \quad \beta_b = \sqrt{\frac{17}{2}} = 2.93 \text{ and } \beta_c = \sqrt{\frac{34}{1}} = 5.83.$$

In other words, reaction (a) is the most probable. After a detailed analysis of the geometry of the process, in which the volume V within which reactions (a), (b), and (c) can occur is expressed in terms of the appropriate value of β, Pucheault finds that $V(a) = 40\,V(b) = 100\,V(c)$. These relative sizes of the reaction region, however, are not borne out by the experimental finding that reactions (a) and (b) have almost identical yields, or by Allen's calculation[82], according to which $K(a) \simeq K(b)$.

Various arguments aimed at explaining these discrepancies are advanced in Pucheault's book[81].

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ELECTRODEPOSITION OF ALLOYS

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I. INTRODUCTION. PHYSICOCHEMICAL PROPERTIES AND APPLICATIONS OF ELECTRODEPOSITED ALLOYS

The evolution of modern technology makes increased demands on the physicochemical properties of metallic surfaces. In several cases they must possess definite properties (corrosion resistance, magnetic properties, high dielectric constant, etc.), and quite often even a combination of such properties. Surfaces having specified properties can be produced by depositing alloys consisting of two or more metals.

The electrodeposition of alloys under conditions of simultaneous discharge of the ions has attracted considerable interest during recent years†. The resulting alloys have wide and varied uses in technology. For example, zinc–cadmium alloys[1] are distinguished by high corrosion resistance in tropical climates, and lead–tin alloys in seawater; alloys based on chromium show improved retention of mechanical properties at high temperatures and are very resistant to oxidation[2-4]; cobalt–nickel alloys have high chemical resistance and hardness, silver–cadmium alloys a high optical reflectivity which does not change with time, and alloys of lead with copper or silver good antifriction properties. Finally, a deposit which has long been known — brass — has recently acquired wide use as a preliminary coating of steel before nickel or chromium plating, and also in the manufacture of shock-absorbers, as an intermediate layer in the application of rubber to steel[5].

Furthermore, under conditions of the codeposition of metals it becomes possible to deposit in an alloy even metals which cannot be obtained in pure form from aqueous solution. It also becomes possible to deposit alloys based on metals of high melting point, for example tungsten[6-17], molybdenum[18-25], and rhenium[26,27]. Such coatings of heat-resistant alloys possess several engineering and economic advantages.

The above properties of electrodeposited alloys, as well as their finely crystalline structure, density, increased hardness, and other properties, have been responsible for their ever extending application in industry. At the present time practical electroplating has been undertaken with alloys based on copper[5,28-33], lead[34-42], nickel[43-47], tin[48-64], and other metals. Methods for electrodepositing alloys of three or four metals have also been developed[14,65-76].

The number of papers published on the electrodeposition of alloys has also increased considerably during recent years. However, most of them deal with applied problems in the development of a formula and the technical conditions for the production of a given alloy. Comparatively few consider questions of the structure of the alloys, the conditions for their electrodeposition, and the kinetics of electrode processes involving the codeposition of metals.

Study of the electrodeposition of one metal is linked with the solution of many individual problems. The complexity of processes involved in the formation and growth of metal crystals by the discharge of ions is responsible for the variety of methods used in their investigation.

In the electrodeposition of alloys, additional difficulties appear, as a result of the simultaneous discharge of two or more types of ions, connected both with the change in activity of the reducible ions in the layer adjacent to the cathode and with the change in nature and state of the cathode surface. In order to ascertain the conditions for the production of alloys, therefore, investigation of the kinetics of electrode processes must be accompanied by a study of the properties of the electrodeposits.

II. STRUCTURE OF ELECTRODEPOSITED ALLOYS

Alloy deposits formed by the simultaneous deposition of metals on a cathode differ considerably in properties from alloys obtained by a thermal method. Electrodeposited alloys are harder, non-homogeneous, and finely crystalline. Considerable interest therefore attaches to investigating the structure of electrodeposited alloys and to ascertaining the extent to which their phase constitution corresponds to the equilibrium diagram. Establishment of the relation between the conditions of crystallisation of the alloys and their properties is also extremely important.

The structure of alloys is usually investigated with X-rays[38,57,77-85]. In several cases alloys obtained by electrodeposition and by the thermal method have identical structure[28,86-92].

The literature also contains references to the ability of electrodeposited alloys to form supersaturated solid solutions. Thus an increased proportion of one component has been observed in alloys whose components are mutually insoluble at low temperatures (for example Cu–Pb[81] and Ag–Pb[38]) and in several other alloys (Pb–Sn[57], Cu–Sn[80], Ag–Tl[91], and Ag–Bi[92]). On the other hand, an alloy belonging to a eutectic type of system (Cd–Zn) consists of a mixture of crystals of each component[93].

Considerable differences in the structure of the same alloys have been observed when they are obtained under different conditions. Depending on the conditions of deposition, Cd–Ag alloys contain solid solutions in some cases[87,89] and three phases (α, β, and γ) in other cases[94], these phases differing in composition from the corresponding phases in cast alloys. Thus electrodeposited alloys quite often differ appreciably in physical and mechanical properties from cast alloys, and are characterised by distortions of the crystal lattice. The phase constitution of such alloys depends on the conditions under which they have been electrodeposited.

From an investigation of the structures of a large number of alloys, Raub[82] concluded that, in the crystallisation of electrodeposited alloys, solid solutions can be formed only when codeposition of the metals already occurs at the lowest current densities. In such a case, the electrodeposited alloys do not differ in structure from cast alloys

† The production of alloys by electrodepositing one metal on a foreign cathode, which is then heat-treated, has not been widely used.

of corresponding composition. If, however, discharge of ions of one of the components begins only when a definite current density has been reached, the alloy consists of a mixture of the components.

The X-ray method does not always yield sufficiently complete information on the structure of electrodeposited alloys. In several cases the X-ray patterns contain diffuse lines, and only a proportion of the phases present in alloys can be determined. As a result, it has become necessary to use indirect methods as well. Combination of data from X-ray and thermographic investigations, density, magnetic properties, and superconductivity at low temperatures makes it possible to determine the phase structure of alloy electrodeposits[95-99]. By the above methods, for example, copper–bismuth alloys deposited at various potentials have been shown to contain a mixture of copper and bismuth crystals (in conformity with the phase diagram), a supersaturated solid solution phase, and a metastable phase of chemical compound type[100].

Gorbunova and Polukarov[101] have examined the mechanism of alloy formation and the dependence of phase structure on electrochemical conditions of deposition for systems characterised by different types of interaction between the components; this represents an extremely promising line of research.

The concepts associated with the formation and growth of a new phase have been enlisted to solve the problem of the mechanism of alloy formation on the cathode. Additional energy is required[102-105] for the formation of a crystal nucleus of a new phase on a foreign metal, and in the case of electrolysis this is represented by an increase in potential immediately after the current has been switched on.

Under the conditions of cathodic alloy deposition, the production of supersaturated solid solutions will obviously be determined to a considerable extent by the difficulty of forming a new phase of the metal which is the more electronegative in the given solution. Here two possible cases are distinguished[101]: (1) the potential of steady deposition is more positive than the potential required for formation of a crystal nucleus of the more electronegative metal, but exceeds its equilibrium potential; (2) the potential of steady deposition of the metal exceeds the potential of nucleus formation. In the former case a homogeneous system — a (supersaturated) solid solution — can be formed. In the latter case, however, the cathodic deposit will consist of a mixture of the components: *i.e.* formation of two-phase systems is possible. If the differences in atomic radius are considerable, inclusion of a second component in the lattice of the more positive metal may result in distortion of the lattice, which in turn requires the consumption of additional energy.

With increase in cathodic overpotential, the energy states of the reduced atoms of the more electropositive metal also change; this produces increased solubility of the second component in this metal with the formation of a supersaturated solid solution phase. Thus the magnitude of the cathodic overpotential has an important effect on the phase constitution of electrodeposited alloys. Therefore alloys containing every possible kind of phase can be formed in the simultaneous electrodeposition of metals on a cathode, independently of the form of the phase diagram. Deposition of the components of an alloy at high overpotentials may result in the formation on the cathode of phases which are not found in the usual equilibrium systems.

The formation of metastable phases, in particular, is of practical interest for the production of magnetically rigid materials of high coercivity. The appearance of such properties in alloys is governed by the size and shape of the crystals of the ferromagnetic phase and by the internal stresses at the interface between solid solution and chemical compound. Among such alloys can be included Co–Ni[106-109] and Co–W[100] electrodeposits, which are applied as coatings in the memory devices of electronic computers and in sound-recording apparatus.

However, the limiting solubility of the components is determined not only by the cathodic overpotential but also by the kinetics of the deposition process, and can therefore be affected by other conditions of electrolysis.

The question of the phase structure of electrodeposited alloys and its dependence on electrochemical conditions of deposition is of considerable interest for the practice and theory of the electrodeposition of alloys, but a more detailed consideration of this topic is beyond the scope of the present review.

III. THERMODYNAMIC CONDITIONS FOR SIMULTANEOUS ELECTRODEPOSITION OF METALS

The possibility of the simultaneous electrodeposition of metals with formation of an alloy on the cathode is governed by definite thermodynamic and electrochemical conditions.

In the case of two metals M_1 and M_2, codeposition can occur when their deposition potentials become equal. Each potential φ can be represented as the sum of two components — the reversible or equilibrium potential φ_{eq} and the polarisation η, which represents the irreversible consumption of energy required to maintain the process at a definite rate:

$$\varphi = \varphi_{eq} - \eta. \qquad (1)$$

The equilibrium potential of a given metal depends both on the activity of the ions undergoing discharge $a_{M^{n+}}$ and on the activity of the metal on the electrode a_M:

$$\varphi_{eq} = \varphi_0 + \frac{RT}{nF} \ln \frac{a_{M^{n+}}}{a_M}, \qquad (2)$$

where φ_0 is the standard electrode potential of the metal. For the deposition of a pure metal on a cathode of the same metal, where the activity of the metal is taken as unity ($a_M = 1$), Eqn. (2) becomes

$$\varphi_{eq} = \varphi_0 + \frac{RT}{nF} \ln a_{M^{n+}}. \qquad (3)$$

If, however, deposition of the metal is accompanied by formation of an alloy on the cathode, the activity of the metal is diminished. From Eqn. (2) the equilibrium potential of the metal may be expected to be more positive under these conditions than when it is deposited on the pure metal cathode. This shift in equilibrium potential to more positive values resulting from a change in the activity of the metal in the alloy is the depolarisation $\Delta\varphi$. Its magnitude can be calculated from the well-known thermodynamic formula

$$\Delta\varphi = -\frac{\Delta\bar{G}}{nF}, \qquad (4)$$

where $\Delta\bar{G}$ is the partial Gibbs free energy of the metal in

the alloy, which is directly related to the change in activity of the metal:

$$\Delta\bar{G} = RT \ln a_M. \quad (5)$$

Simultaneous solution of Eqns. (4) and (5) gives an expression for the depolarisation:

$$\Delta\varphi = -\frac{RT}{nF} \ln a_M, \quad (6)$$

from which it follows that the depolarisation must be expected to increase as the activity of the metal in the alloy decreases.

In general the activity of a metal in an alloy is determined not only by the composition of the latter but also by the nature of the interaction between the components accompanying alloy formation[110]. Hence alloys having the same proportions of the components but different types of interaction may show different amounts of depolarisation. The different cases of change in depolarisation enumerated below can be distinguished[111] in the cathodic formation of liquid alloys.

1. Ideal solutions, in which the activity of a metal is equal to its atomic fraction ($a = N$). From Eqn. (6) the magnitude of the depolarisation in this case is obviously

$$\Delta\varphi = -\frac{RT}{nF} \ln N. \quad (7)$$

Curve *1* in Fig. 1 represents calculated values for a univalent metal at 600°.

2. Solutions showing considerable negative deviations from Raoult's law. Such deviations are explained by strong interaction between the components with formation of structural clusters of intermetallic compounds in the liquid alloys. When compounds are present in alloys, the activities become less than the corresponding atomic fractions ($a_M < N_M$). In this case, as the activity of a component in the alloy decreases, the depolarisation will increase and exceed the corresponding value for an ideal solution. For example, the dependence of depolarisation on composition for the K–Pb system[112] is represented by curve *2* in Fig. 1. The most stable compound in this system is regarded as KPb with m.p. 578°.

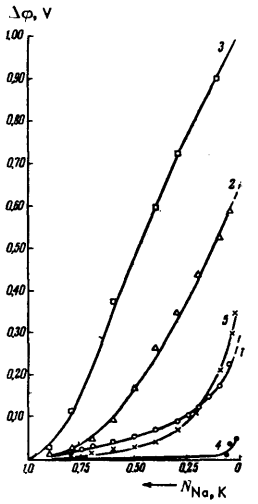

Fig. 1. Dependence of depolarisation on composition of liquid alloys:
1) ideal solution; 2) K–Pb; 3) K–Bi; 4) Na–Zn; 5) Na–Cd.

Systems in which yet more stable compounds are formed show a greater divergence of the depolarisation from the ideal value. Thus the dependence of $\Delta\varphi$ on composition for the K–Bi system[113], which forms K_3Bi (m.p. 671°) as the most stable compound, is shown by curve *3* in Fig. 1.

3. Solutions characterised by positive deviations from Raoult's law must be expected to exhibit less depolarisation than do ideal solutions. Positive deviations in activity are usually observed in alloys in which mixing of the components is accompanied by the absorption of heat, and are due to the existence of structural clusters of the pure metal. Curve *4*, representing the variation in the depolarisation of sodium in Na–Zn solution[114], lies below the curve for ideal solutions (Fig. 1).

4. Solutions characterised by positive and negative deviations from Raoult's law exhibit a complicated variation of depolarisation with composition. Such deviations in the activity of one of the components are observed when structural clusters of unsymmetrical compounds are formed[115] in the liquid solution. Examples are provided by K–Hg[116] and Na–Cd[117] solutions, the variation of $\Delta\varphi$ with composition in the latter example being plotted as curve *5* in Fig. 1.

Simultaneous discharge of the ions of two metals may also result in the formation on the cathode of an alloy in which the components are mutually insoluble and do not form compounds. In this case, the activities of both metals obviously remain unchanged, and there should be no resultant shift in the deposition potentials of the components. In the codeposition of lead and copper[118], whose mutual solubility in the solid state can be regarded as zero[119], appreciable depolarisation of the components compared with their separate deposition is not in fact observed.

For several alloys the magnitude of the depolarisation can be determined from experimental data obtained in the thermodynamic investigation of the alloys.

Methods are described in the literature[110,120] for determining the partial Gibbs function of the components of an alloy of specified composition. Tables of data usually contain integral values of the function. The latter can be converted into the partial values by one of the published methods, either by differentiation or graphically[121]. The latter procedure has been examined in detail for an alloy whose components form a continuous series of solid solutions[122,123]. The absolute value of the partial Gibbs function of each component in the alloy may considerably exceed the corresponding value of the integral function. It falls with increasing content of the given component in the alloy, while the corresponding value for the second component increases, reaching a maximum when atoms of one component are mixed with the pure second component.

Fig. 2 shows plots based on published data[124] of the variation in the partial Gibbs function of solid zinc and copper on dissolution in the solid alloys.

Alloys containing both homogeneous and heterogeneous regions show deviations from a smooth curve. In this case the relation is represented by a broken line, as in Fig. 3. Here the value of $\Delta\bar{G}$ remains unchanged in the sections representing heterogeneous systems containing two components in varying proportions.

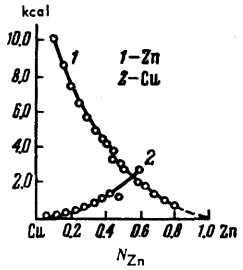

Fig.2. Dependence of partial Gibbs free energy for components on alloy composition: 1) zinc; 2) copper.

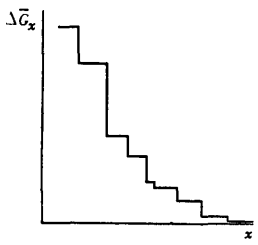

Fig.3. Variation in Gibbs free energy in alloy containing heterogeneous regions.

Thus it follows from a consideration of the thermodynamic conditions for the simultaneous electrodeposition of metals that, in all cases of alloy formation, depolarisation of each component is to be expected owing to the change in its energy state. The magnitude of the depolarisation is determined by the form of the interaction between the components in the alloy, and can be either greater or less than the theoretical value.

It must be remembered, however, that determination of the shift in the equilibrium potential caused by the change in the energy state of a metal in a solid alloy is complicated by several factors. The depolarisation can be determined directly only when liquid alloys are deposited on the cathode, where the conditions of their formation permit the practical achievement of equilibrium conditions.

IV. ELECTROCHEMICAL CONDITIONS FOR SIMULTANEOUS ELECTRODEPOSITION OF METALS

Examination of electrochemical processes has established that two metals can be deposited together on a cathode provided that they have the same deposition potential:

$$\varphi_{eq,1} - \eta_1 = \varphi_{eq,2} - \eta_2. \qquad (8)$$

It follows from Eqn. (8) that equality of the deposition potentials of two metals can be achieved by changing either equilibrium potential φ_{eq} or polarisation. Substitution of Eqn. (2) in Eqn. (8) gives

$$\varphi_{0,1} = \frac{RT}{n_1F}\ln\frac{a_{M^{n_1}}^{+}}{a_{M_1}} - \eta_1 = \varphi_{0,2} + \frac{RT}{n_2F}\ln\frac{a_{M^{n_2}}^{+}}{a_{M_2}} - \eta_2. \qquad (9)$$

Thus simultaneous discharge of two types of ions requires definite relations between the activities of the ions in the electrolyte, the activities of the metals in the alloy, and the overpotentials under the conditions of their codeposition. Let us examine the ways in which each of these factors can vary.

One method for equalising the deposition potentials of metals is to vary the activities of their ions in solutions of their simple salts. However, only a slight shift in the potential can be achieved in this way (a tenfold change in the activity of a univalent ion produces at room temperature a change in the equilibrium potential of 58 mV, the corresponding change for a bivalent ion being 29 mV). Therefore such a method can be used only in the codeposition of metals having similar standard electrode potentials, for example Co–Ni[125] and Sn–Pb[126].

An extremely effective method for varying the activity of ions is to incorporate them into complex ions, when both the activity of the ions in the solution and the kinetic conditions of their discharge are changed[127–130]: *i.e.* both the equilibrium potential and the polarisation are affected. By complex formation it is therefore possible not only to bring the deposition potentials of metals closer together but even to change their relative positions. This procedure is used in practice for the production of alloys whose components differ considerably in standard potential, for example Cu–Zn[29,30,33,131–134], Cu–Sn[51,52,55,56,60,135], Sn–Ni[44,61,63], Sn–Zn[53,62,65,136,137], Zn–Cd[138,139], Zn–Ni[140], Cu–Ni[47,141,142], Ag–Au[143,144], Cu–Au[145–147], Ag–Pb[37,148], etc.

Codeposition of two metals can be effected also under conditions of a limiting current of the more positive metal. In this way Zn–Cd[139] and Cu–Pb[118] alloys have been obtained from solutions of their simple salts. Investigation of the cathodic deposition of copper–lead alloys has revealed that the proportion of the current involved in the deposition of copper reaches practically the same limiting value in the presence of various additives (HNO_3, KNO_3, NH_4Cl, and $H_6C_4O_6$) at different cathode potentials. Simultaneous deposition of lead and copper takes place close to the deposition potential of pure lead, and under conditions of a limiting current of the copper. The fraction of the current due to the deposition of copper increases to values considerably exceeding the limiting current of copper in the absence of lead. This increase is explained by intensified convection of the solution near the cathode during the discharge of the heavy lead ions, as a result of which the supply of copper ions from the solution to the cathode surface is increased.

In this case the proportion of copper in the deposit is determined, for a given concentration of its ions in the solution, by the conditions governing their diffusion to the cathode surface. In conformity with the equation derived by Kheifets and Rotinyan[149], it can be assumed that

$$C_{Cu} = \frac{D[Cu^{2+}]}{i_{Pb}}, \qquad (10)$$

where C_{Cu} is the percentage of copper in the deposit and D the diffusion coefficient.

Thus under these conditions the composition of the deposit is independent of the cathode potential, and can be

controlled by varying the current density i_{Pb} involved in the deposition of lead.

It is usually supposed that the production of alloys under conditions of a limiting current of one of the components results in deposits of unsatisfactory quality. It has been shown[118] that the quality of a deposit is determined by the relative quantities of the components deposited on the cathode. Dense, finely crystalline deposits can be obtained only by the discharge of ions of the more electropositive metal into a dense mass of the other metal. In the case of copper–lead alloys, satisfactory deposits have been obtained at current efficiences of lead deposition which do not fall below 50%.

A second condition for the simultaneous deposition of metals which follows from Eqn. (9) is the presence of definite relations between the activities of the metals in the alloy. The chief aspects of this condition have been discussed in Section III, but here it must be remembered that alloy formation on a cathode can also occur by interaction between a deposited metal and the material of the cathode. In the deposition of a metal on a liquid cathode, the depolarising action of the cathode material is exhibited continuously, owing to the continual renewal of the surface by diffusion of the resulting alloy into the interior of the cathode. The magnitude of the depolarisation will then obviously be determined by the nature of the interaction accompanying alloy formation.

In practice alloy formation between a deposited metal and the cathode material is realised in the deposition of the alkali metals on a mercury cathode and in the electrolysis of molten salts with liquid metal cathodes. With a solid cathode, however, the depolarising action of the cathode material disappears owing to enrichment of the cathode surface with the deposited metal. In this case the cathode potential is low at the beginning of the process, and subsequently rises.

Finally, a third condition is variation in the overpotential under the conditions of electrodeposition of an alloy. The condition of the cathode surface during electrolysis may produce either an increase or a decrease in the overpotential. Thus during the codeposition of molybdenum and nickel an increase in the nickel overpotential has been observed[150] caused by enrichment of the alloy with molybdenum.

The temperature dependence of the overpotential can also be used to vary the conditions of the simultaneous deposition of metals. If a high overpotential of the more electronegative metal prevents simultaneous discharge of the ions at low temperatures, its decrease with rise in temperature may make electrodeposition of an alloy possible. If, however, the high overpotential characterises the more electropositive metal, a rise in temperature may shift its potential and upset the process of codeposition. However, the magnitude of the overpotential will have an appreciable effect on the displacement of the potentials of the few metals whose deposition is accompanied by considerable overpotential. With most metals, which are characterised by low overpotential, it can be expected that the overpotential will be low under conditions of simultaneous electrodeposition.

The conditions under which ions are discharged can be varied also by adding surface-active compounds to the electrolyte. Such additions are made in industrial electrodeposition to improve the quality of the metal deposit. The mechanism of their action has been examined in several papers. One of the first explanations of the effect of surface-active compounds, in particular of colloids, was given by Izgaryshev and his coworkers[151–154], who assumed it to be due to the formation of colloidal ionic complexes, discharge of which on the cathode occurred with difficulty compared with the discharge of the usual hydrated ions.

Later work showed[155–165] that the change in the structure of the deposits and the increase in polarisation of the electrode occurring in the presence of surface-active additives are due to adsorption of such substances on the cathode surface. The current can then remain constant over a wide range of potentials. Comparison of the polarisation curves with the capacitance of the electrode showed that the current increases over the potential range within which the maximum of the capacitance curve occurs: *i.e.* a low limiting current is observed only within the region where the organic compound is adsorbed[166–168].

The relation between the rates at which surface-active compounds are adsorbed and at which metals are deposited is of considerable significance in electrodeposition. Depending on this relationship, two possible types of effect of surface-active agents can be distinguished: (1) if the rate of adsorption of the surface-active compound is less than the rate of formation of a fresh metal surface, crystal nuclei can be formed only at isolated, unpassivated sites on the electrode[164,169,170]; the electrode polarisation will then vary with change in the true current density, but remain unchanged overall; (2) if, however, the rate of adsorption is sufficiently high, ions can be discharged only after they have penetrated the adsorbed layer, which requires an energy of activation whose magnitude is determined both by the nature of the ion and by that of the adsorbed layer. In the latter case the kinetics of the overall process[157–163] is governed by the stage preceding the actual discharge, which also explains the appearance of a practically constant limiting current. Deposits obtained under these conditions are distinguished by their uniformity.

The selective action of such adsorbed layers for ions of different metals is of especial interest, and governs the possibility of their codeposition with alloy formation on the cathode. Thus in the presence of gum-arabic and cresolsulphonic acid it becomes possible to deposit copper, zinc, and nickel together from a solution of their simple salts[171]. In the cathodic deposition of copper–lead and copper–tin alloys from simple salt solutions in the presence of surface-active substances, copper is deposited[172] first, and the quantity of the second metal deposited then increases with rise in the cathode potential. In this way it has proved possible to obtain finely crystalline, dense deposits containing up to 80% of tin.

Alloys of tin with bismuth[173] and antimony[64] have been obtained in the presence of added glue and crude phenol. The influence of surface-active additions on the deposition of tin–nickel alloys has also been studied[174].

Addition of surfactants to the electrolyte has been used also to obtain bright deposits of several alloys. Thus bright alloys of gold and copper, requiring no subsequent polishing, have been obtained from a cyanide electrolyte in the presence of thiourea[146].

The electrochemical conditions discussed above for bringing the deposition potentials of the components of an alloy close together cover only some of the most thoroughly investigated relations. In practice, the conditions determining the kinetics of the simultaneous discharge of ions

may differ from those occurring in separate deposition owing to changes in several factors, which will be considered in the following Sections.

V. METHODS OF INVESTIGATING AND LAWS GOVERNING THE SIMULTANEOUS DISCHARGE OF METAL AND HYDROGEN IONS

The phenomenon of the simultaneous discharge of ions is widely disseminated in electrochemical technology. Although it is undesirable in some cases (for example, the discharge of hydrogen ions or of ions of other metals in the production of a pure metal), in the deposition of alloys simultaneous discharge is the main process, investigation of which enables the physicochemical properties of alloys to be linked with their composition and the conditions under which they are obtained. Therefore examination of the polarisation accompanying, and the laws governing, the simultaneous discharge of ions is of considerable theoretical and practical interest. Theoretical investigation of these questions forms at the present time a complicated and little studied branch of electrochemistry.

Two types of ions are usually discharged at different rates at a given potential. Two cases can be distinguished depending on the relation between these rates of discharge. In case (1) the rate of discharge of one type of ions considerably exceeds that of the others. It occurs in the refining of metals, and investigation of its laws solves the problem of obtaining metals in a high degree of purity [149,175-178]. In case (2) the two types of ions are discharged at comparable rates. It can be realised either in the simultaneous deposition of two metals with formation of an alloy on the cathode, or in the deposition of one metal accompanied by appreciable hydrogen evolution.

The laws governing such simultaneous processes were investigated by Esin and his coworkers [179-185]. These workers derived an equation for the distribution of current between two types of ions undergoing simultaneous discharge, based on the hypothesis that the rate of discharge of ions is determined by the rate of electron transfer and by concentration polarisation. Tests of the equation on the simultaneous discharge of copper and zinc, nickel and hydrogen, and zinc and hydrogen showed satisfactory agreement between calculated and experimental results in all cases.

During recent years a method has been worked out for investigating the simultaneous discharge of ions which makes it possible to determine the rates of deposition of each component [125,186-192]. In order to explain its principle, we must first consider the peculiarities of such processes. In the discharge of ions of one type the electrode process is usually characterised by the relation between potential and current density at the electrode. When two or more types of ions are undergoing simultaneous discharge at a given potential, the current through the cathode is given by the sum of the partial currents, *i.e.* the currents due to discharge of the corresponding ions:

$$i_{total} = i_1 + i_2 + i_3 + \ldots \qquad (11)$$

In this case the polarisation curve is an aggregate curve representing the whole set of processes occurring at the cathode. Its displacement on passing from the deposition of pure metals to the deposition of an alloy may be governed by the simultaneous operation of several factors, and the effect may be different for each type of ions. For example, a change in the state of the cathode surface under conditions of simultaneous metal deposition and hydrogen evolution will produce a change in the hydrogen overpotential, which in turn would tend to change the proportion of the current due to hydrogen. In the codeposition of metals a change in the conditions of discharge can also produce different changes in the rate of deposition of each component. Furthermore, as already shown in Section III, the depolarisation of each metal depends on its energy state in the alloy. Therefore plotting the aggregate polarisation curve without taking into account the fraction of the current due to deposition of each component may lead to a view of the deposition of a given metal which is not always correct. It has been necessary to dwell on this question, since in several papers [13-15,25,33,62] the depolarisation of the components accompanying alloy deposition has been assessed from the displacement of the aggregate polarisation curves.

The kinetics of electrode processes involving simultaneous discharge of ions can be investigated only by comparing polarisation curves representing the dependence of the deposition rate of a given component on the cathode potential, such curves being termed partial polarisation curves. In the deposition of alloys such partial curves are plotted from analyses of deposits obtained at a given potential. Comparison of partial polarisation curves obtained for separate and simultaneous deposition of metals can give either the change in rate of deposition at a given potential or the shift in potential at a given current density. However, theoretical interpretation of partial polarisation curves is a matter of considerable difficulty, since accurate reproduction of experimental conditions is impossible for deposition of a metal in an alloy and in the pure form.

Rotinyan and Molotkova [191] have made a careful examination of the polarisation curve method in the case of the electrodeposition of Fe–Co alloys, and have shown that three methods can be used to compare polarisation curves. One consists in comparing a partial curve under conditions of simultaneous deposition with the curve for deposition of the pure metal from a solution containing an added inert electrolyte at a concentration equivalent to that of the second component to be deposited. This ensures that the ions of the test component should be at the same activity under conditions of separate and simultaneous deposition. However, the presence of the foreign ions leads to fresh difficulties. Thus addition of $MgSO_4$ produced an inflection on the polarisation curve of cobalt, obviously owing to the recharging of the electrode surface in the vicinity of the zero-charge potential. The displacement of the polarisation curve to more negative potentials is explained by the accumulation of magnesium ions in the outer part of the double layer, which screen the electrode surface and impede the discharge of cobalt ions. As a result, additional polarisation must be provided for the metal to be deposited under these conditions.

The second method of comparison involves deposition of the metals from solutions having the same total concentration of dischargeable ions. In this case the activity coefficient is maintained constant, but the activity of the dischargeable ions varies. The displacement of the polarisation curves is governed solely by the replacement of dischargeable ions of one metal by an equivalent quantity of the other.

In the third method the polarisation curves are compared at equal concentrations of ions of the deposited metal in pure and mixed electrolytes. If the variation in the activity coefficient of the dischargeable ions is slight under

these conditions, this method gives the most accurate values for the shift in the polarisation curves.

It has been shown experimentally [191] that, at relatively high concentrations of a component in a mixed electrolyte, all three methods of determining the displacement of the polarisation curves give similar results. At low concentrations of the ions to be deposited, however, the quantitative shift in the polarisation curves depends on the method of comparison. Nevertheless, the qualitative direction of the shift is the same in all these methods.

Examination of the partial polarisation curves makes it possible to establish the laws of the simultaneous discharge of ions and the nature of the polarisation for each component.

It can now be accepted as established that the deposition of many metals involves a stage of slow discharge of their ions [127,193-195]. Several investigations have also shown [125,190-192,196-200] that the character of the polarisation of each metal remains unchanged on passing to conditions of codeposition. In this case the relative rates of the simultaneous discharge of two types of ions can be expressed by an equation derived by Kheifets and Reishakhrit [186] from the slow discharge theory

$$\frac{A_1}{A_2}=\frac{i_1}{i_2}=\frac{k_1a_1}{k_2a_2}e^{\frac{U_2^0-U_1^0}{RT}+\frac{(\alpha_2n_2-\alpha_1n_1)F}{RT}\varphi}, \qquad (12)$$

where, for the two types of dischargeable ions, A represents the current efficiency expressed as a fraction, a the activity of the dischargeable ion adjacent to the cathode, U^0 the activation energy of the ions at the zero-charge potential, and i the fraction of the current involved in deposition of the given component, the remaining symbols having their usual significance.

Taking logarithms, we obtain from this equation

$$\log\frac{i_1}{i_2}=\log\frac{k_1}{k_2}+\log\frac{a_1}{a_2}+\frac{U_2^0-U_1^0}{2.3RT}+\frac{(\alpha_2n_2-\alpha_1n_1)F}{2.3RT}\varphi. \qquad (13)$$

Eqn. (13) yields particular relations between $\log i_1/i_2$ and $\log a_1/a_2$, T, and φ for constant values of the remaining quantities, for example.

$$\log\left|\frac{i_1}{i_2}\right|_{T,\frac{a_1}{a_2}}=\frac{(\alpha_2n_2-\alpha_1n_1)F}{2.3RT}\varphi+\text{const}. \qquad (14)$$

It is evident from Eqn. (14) that under the given conditions a linear relation should be observed between the potential and $\log i_1/i_2$.

In the codeposition of two metals uncomplicated by hydrogen evolution, a rise in cathode potential must be expected to be accompanied by an increase in the proportion of the more electronegative component. In fact, the composition of Co–Mo [18], Co–Ni [125], Sn–Pb [126], and Cr–Ni [201] deposits vary steadily with change in current density (or potential).

Increase in potential must also increase the current efficiency of metal deposition and decrease $\log i_H/i_M$ in the simultaneous deposition of a (bivalent) metal and evolution of hydrogen, when $\alpha_M n_M > \alpha_H n_H$. In the simultaneous deposition of zinc and evolution of hydrogen from strongly acid solutions [202,203], however, the increase in current efficiency of zinc deposition slows down at a definite potential, and the relation between $\log i_H/i_{Zn}$ and φ ceases to be linear [200].

These deviations have been explained [200] on the basis that the activities of the dischargeable ions in the cathode layer, occurring in Eqn. (13), are unknown during electrolysis, so that the ionic activities in the bulk of the solution are usually employed in calculations. However, ionic activities in the solution adjacent to the electrode are changed by the passage of the current, and may differ considerably from the activities of the corresponding ions in the rest of the solution. The activity of each type of ion in this layer is determined, on the one hand, by the rate of discharge at the cathode and, on the other, by the rate of supply of these ions from the solution to the cathode layer. The rate of discharge may then either exceed the rate of supply or lag behind it. Let us consider each of these cases.

In the simultaneous deposition of a metal and evolution of hydrogen from strongly acid solutions, when the rate of supply of hydrogen ions to the cathode exceeds their rate of discharge, the ensuing increase in acidity adjacent to the cathode must diminish the current efficiency of metal deposition. The rate of deposition of the metal must also fall in comparison with its rate of separate deposition, as a consequence of the partial replacement of metal ions by hydrogen ions in the cathode layer. In this case a decrease in the current efficiency of metal deposition and an increase in the value of $\log i_H/i_M$ must be expected, as have in fact been observed [202,203].

Considerably more complicated phenomena are observed when the rate of supply of hydrogen ions lags behind their rate of discharge. This case can occur in weakly acid solutions. According to Eqn. (13), the decrease in acidity of the cathode layer which occurs under these conditions must result in an increased efficiency of metal deposition. In addition, a rise in cathode potential will be accompanied by an increase in the difference in pH between the cathode layer and the bulk of the solution.

In the presence of salts of metals capable of forming sparingly soluble hydroxides or basic salts, the rise in pH in the cathode layer is limited by the pH at which these compounds are formed under the given conditions [204-208]. Formation of such compounds produces a sharp decrease in the activity of metal ions in the cathode layer, and this in turn leads to a diminished rate of discharge. As a result of these phenomena, the current efficiency of metal deposition must decrease, and the distribution of the partial currents due to hydrogen and the metal change.

Experimental investigation of the kinetics of the deposition of nickel [186] and of zinc [200] accompanied by hydrogen evolution has shown that under these conditions the process of metal deposition is in fact complicated by concentration phenomena. Similar phenomena can be expected also in the simultaneous deposition of two metals and evolution of hydrogen, which occur in many cases of the practical electrodeposition of alloys. Therefore the investigation of cathodic processes under these conditions is of considerable interest.

As a result of hydrogen evolution, the pH at the cathode may reach the value required for hydroxide formation by one of the metals, but which is insufficient for the second hydroxide. Then, as already shown above, the current efficiency for the first metal must be expected to diminish, whereas that for the second metal will increase until a definite potential is reached.

The above principles have been confirmed experimentally by an investigation of the electrodeposition of copper–

zinc alloys from oxalate electrolytes[199]. Figs. 4*a* and 4*b* show the dependence of the current efficiencies for zinc and copper deposition on potential under conditions of co-deposition. Whereas the efficiency of copper deposition steadily diminishes with rise in potential, that of zinc deposition increases to a definite "critical" [199] value, and it is only when such a potential is reached that the yield of zinc drops sharply. This difference in variation of current efficiency between copper and zinc is obviously due to the different pH values of hydroxide formation, 4.5 for $Cu(OH)_2$ and 5.9 for $Zn(OH)_2$.[204,205] Owing to the lower pH required, copper hydroxide is formed (though this may not be perceptible) from the very start of electrolysis. In the case of zinc the pH of hydroxide formation can be reached only with definite relative rates of zinc deposition and hydrogen evolution, *i. e.* at definite cathode potentials.

When these "critical" potentials are reached, the polarisation of zinc and copper becomes identical in character (Fig. 5). The partial polarisation curves have similar slopes in semilogarithmic coordinates. Then $\alpha_{Cu}n_{Cu} \simeq \alpha_{Zn}n_{Zn}$, and the distribution of partial currents should not be affected by change in potential in this case, as follows from Eqn. (14). The correctness of this view is confirmed by the curves in Fig. 4*c*.

It obviously follows that the composition of the alloy, too, will vary only up to the same potentials. Fig. 4*d* shows that, under conditions of the simultaneous discharge of copper, zinc, and hydrogen, the production of alloys of variable composition is possible only up to "critical" values of the potential. When these are reached, the composition

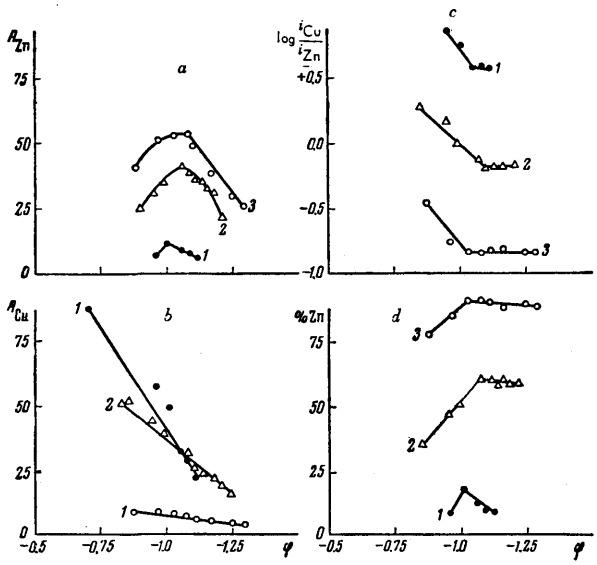

Fig.4. Dependence on cathode potential of: *a*) current efficiency of zinc deposition; *b*) current efficiency of copper deposition; *c*) distribution of partial currents; *d*) composition of copper–zinc alloy; for solutions containing (M):

	$ZnSO_4$	$CuSO_4$	$K_2C_2O_4$	H_3BO_3
1)	0.0056	0.020	0.187	0.324
2)	0.0156	0.010	0.187	0.324
3)	0.024	0.0016	0.187	0.324

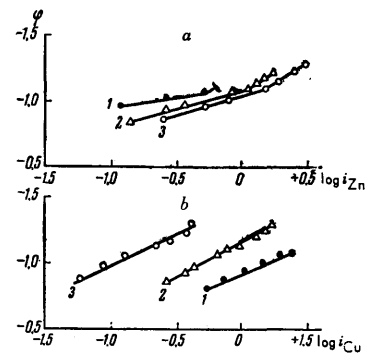

Fig.5. Partial polarisation curves obtained under conditions of codeposition of: *a*) zinc; *b*) copper. Composition of solutions as in Fig.4.

of the alloy deposits remains practically constant, except in the case of alloy No. 1, which was deposited from solutions having a very low concentration of zinc salt.

A similar type of variation in composition with change in cathode potential can be observed in the deposition of other alloys accompanied by hydrogen evolution, for example of Sn–Zn,[209] Ag–Pb,[37] Cu–Au,[146] and Cu–Zn from cyanide solutions[32,131].

From the investigation of the kinetics of metal deposition with alloy formation it can be concluded that, in both strongly and feebly acid solutions, the simultaneous evolution of hydrogen is responsible for the variation in the laws governing the simultaneous discharge of metal ions.

VI. DEPOLARISATION AND SUPERPOLARISATION OF ALLOY COMPONENTS

As shown above, alloy formation must be expected to involve depolarisation of the deposition of each component. However, comparison of partial polarisation curves by the above methods has established that, under conditions of the cathodic formation of alloys, deposition of one component may be facilitated (depolarisation) and at the same time that of the other component may be retarded (superpolarisation).

From a study of the conditions producing a shift in the potential during codeposition of metals characterised by chemical polarisation, Rotinyan and Molotkova[198] concluded that all theoretically possible cases of displacement of the partial polarisation curves — representing positive, negative, or zero depolarisation — could occur in cathodic alloy formation.

In the experimental investigation of the electrodeposition of various alloys (Co–Ni[125], Cu–Zn[131,190], Sn–Zn[209], Sn–Pb[126], Sn–Sb[64], Cu–Ni[140,210,211], Ni–Co[196], Fe–Co[198,212], Fe–Ni[197,212], Mo–Ni, and W–Ni[24]), depolarisation of the more electronegative components and superpolarisation of those deposited at the greater rate have been observed independently of the type of interaction between the components.

It has been shown above (Section III) that the phenomenon of depolarisation is determined by the thermodynamic conditions of alloy formation, *i.e.* by the change in the energy state of the metal in the alloy.

Superpolarisation of one of the components is obviously due to other factors which may appear under conditions of the simultaneous discharge of ions or the formation of a solid alloy. These factors will be considered below.

Production of a solid alloy on the cathode may be assumed to be complicated by processes associated with formation of a new type of crystal lattice. The structure of the latter is determined by the type of interaction between the alloy components[213]. Thus in the case of solid solutions the lattice of the quantitatively predominant component of the alloy is usually preserved, the atoms of the second component "taking root", as it were, in the lattice of the first, and merely changing the size of the unit cell. If the alloy contains intermetallic compounds, it forms a lattice which differs from those of the initial components. Finally, when a eutectic type of alloy crystallises, lattices may appear which are similar to those of the pure components (in the extreme ranges of composition) and resemble those of intermetallic compounds (in the regions of formation of the eutectic).

Thus, from the formation of different types of crystal lattices with different alloys, a different change in magnitude and direction of the shift in the partial curves of the components could be expected in each individual case. If it is postulated that superpolarisation (or depolarisation) of the component is caused by change in the lattice constant with variation in composition of the alloy, a definite relationship could also have been expected between them. In the deposition of Co–Fe alloys, however, the lattice constant was found to change sharply at a definite alloy composition[85], while the superpolarisation of cobalt and the depolarisation of iron vary smoothly[198].

It is clear from the above that no direct relation can be observed between superpolarisation and the type of lattice formed.

The cause of superpolarisation may be the change in the conditions of ionic discharge on passing from separate to simultaneous deposition of the components. According to Vagramyan and Fatueva[196,197,212] these conditions include change in ionic concentration adjacent to the cathode caused by the displacement of some ions by others, increased adsorption of hydrogen and the resulting hydroxides on the cathode surface, change in condition of the electrode surface (in its degree of passivation), and the consequent change in overpotential of the metals.

In actual combined systems the mutual influence of the ions undergoing discharge adjacent to the cathode leads to a breakdown in the kinetic laws established for the individual electrode reactions. In this case the condition of simultaneous discharge, Eqn. (9), can be written[180]

$$\varphi_{0.1}+\frac{RT}{nF}\ln C_1-\frac{RT}{nF}\ln\frac{\Sigma\alpha_i C_i}{\alpha_1 C_1}-\eta_1^{all}=\varphi_{0.2}+\frac{RT}{nF}\ln C_2-\frac{RT}{nF}\ln\frac{\Sigma\alpha_i C_i}{\alpha_2 C_2}-\eta_2^{all}, \quad (15)$$

where C_i is the concentration of each type of ions, and α a coefficient representing the ability of the given type of ions to penetrate the electrical double layer. The term

$$\frac{RT}{nF}\ln\frac{\Sigma\alpha_i C_i}{\alpha_1 C_1},$$

then represents the decrease in polarisation due to entry of other ions into the double layer.

On testing these assumptions in the electrodeposition of the alloys Co–Ni[196], Ni–Fe[197], and Co–Fe[212], the above workers observed an anomalous increase in the rate of reduction of the more electronegative component (Fe) accompanied by a decrease in the rate of reduction of the more electropositive component (Co or Ni). They explained the observed phenomena by the change in overpotential of metal deposition accompanying codeposition and resulting from the change in the nature of the electrode layer.

In the codeposition of nickel and cobalt the rates of reduction of both types of ions were strongly retarded[196]. Careful investigation of this phenomenon revealed that the retardation of simultaneous reactions was far greater than could have been expected solely from the change in concentration of the dischargeable ions in the double layer, and it was therefore suggested that other causes might be operating, namely a change in the state of the ions in solution and a change in the state of the electrode surface and its tendency to become passivated.

Superpolarisation of one component has been observed also in the above case of simultaneous zinc deposition and hydrogen evolution from strongly acid solutions[202,203]. As in all other cases, superpolarisation was observed with the component which separated at the greater rate, which in this system was zinc. It must be noted that here the nature of the electrode surface does not change, no hydroxides are formed, and the zero-charge potential of the zinc remains[214] unchanged.

A similar phenomenon has been observed[192] on passing from the evolution of hydrogen from a pure dilute acid to its evolution accompanied by deposition of an iron–cobalt alloy from solutions having the same pH values. The polarisation of hydrogen under these conditions is due to a slow ion-discharge step. At low temperatures, however, concentration polarisation is observed at sufficiently high current densities. The hydrogen limiting-current plateaux are then considerably lower in the presence of metal deposition than for evolution from acid.

This general presence of superpolarisation (or retardation of the rate of reduction) in the codeposition of different metals and even in simultaneous metal deposition and hydrogen evolution suggests that it has the same cause in all cases. The most probable is the mutual influence of the dischargeable ions, resulting in a change in the electrochemical conditions for their codischarge. This problem has been examined[215] for the simultaneous deposition of metals when the slow stage is the discharge of their ions.

The rate of deposition of a pure metal can be represented by the equation

$$i_M = k_M \times a_M e^{-\frac{U}{RT}} \times e^{\frac{\alpha_M nF}{RT}(\varphi_M^0-\varphi)}, \quad (16)$$

in which φ_M^0 is the zero-charge potential, and all the other symbols have the same significance as in Eqn. (12). The rate of deposition of the same metal under codischarge conditions can be expressed by a similar equation but with the subscript c attached to the symbols. Simultaneous solution of the two equations yields[215] the expression

$$\ln\frac{i_c}{i_M}=\ln\frac{k_c}{k_M}+\ln\frac{a_c}{a_M}-\frac{U_c^0-U_M^0}{RT}+\left[\frac{\alpha_c nF}{RT}(\varphi_c^0-\varphi)-\frac{\alpha_M nF}{RT}(\varphi_M^0-\varphi)\right]. \quad (17)$$

The quantity i_c/i_M represents the change in rate of deposition of the metal on passing from separate to simultaneous deposition at a given potential. Increase in the rate of deposition of the metal in the alloy ($\ln i_c/i_M > 0$) defines depolarisation, and a decrease ($\ln i_c/i_M < 0$) represents superpolarisation.

It follows from Eqn. (17) that the change in the value of $\ln i_c/i_M$ is determined primarily by the change in properties of the cathode surface when the alloy is deposited on it (if $\varphi_c^0 \neq \varphi_M^0$), by the change in activity of the dischargeable ions in the layer adjacent to the cathode, and by the change in the coefficient α_c compared with α_M.

The change in properties of the cathode surface is exhibited in particular in a shift in the zero-charge potential. No data on such potentials for different systems are available in the literature, and therefore it is not yet possible to assess sufficiently fully the way in which φ_c^0 depends on the type of interaction between the components. It is known merely that, in solid solutions [216] and amalgams [217,218], diminution in the content of the component possessing the more positive zero-charge potential produces a rapid shift in the latter to more negative values, approaching the value of φ^0 for the second component.

It follows from Eqn. (17) that a change in zero-charge potential of an alloy can have different effects on the displacement of the partial curves of each component. If the zero-charge potential of the pure metal is more negative than φ^0 for the alloy, the fourth term on the right-hand side of Eqn. (17) will, under otherwise identical conditions, become positive, resulting in depolarisation of this component. For a metal having a more positive φ^0, transition to codischarge conditions produces a change in the zero-charge potential which will cause superpolarisation.

As shown above, the change in activity of the dischargeable ions adjacent to the cathode is governed by their relative rates of discharge and of supply from the solution. Since under the conditions of simultaneous discharge of the ions of two metals their rates of supply may be very similar, the activities of the ions in the cathode layer will obviously be determined mainly by the difference in rates of discharge. If the rate of deposition of a given metal M_1 exceeds the rate of deposition of the second metal M_2, ions of the latter $M_2^{n_2+}$ will accumulate in the cathode layer during electrolysis, partly replacing the $M_1^{n_1+}$ ions. The diminished activity of these latter ions thus results in a decrease in the value of $\ln i_c/i_{M_1}$ in Eqn. (17): *i.e.* it leads to superpolarisation of M_1.

In practice it has been found that the rate of deposition of a pure metal is slowed down also by addition of inert electrolytes [191,219]. In addition to concentration phenomena, increased activation energy of discharge U^0 of the metal ions has been observed [219]. Under conditions of simultaneous discharge, the increase in U_1^0 produces an increase in absolute magnitude of $(U_c^0 - U_M^0)/RT$ in Eqn. (17), which may result in superpolarisation.

The rate of deposition of a metal must be affected in a different way by the introduction of ions having a greater rate of deposition. It is obvious that in this case the rapidly dischargeable ions cannot retard to any appreciable extent deposition of the other metal.

The change in the coefficients α on passing from separate to simultaneous metal deposition has been determined for a few alloys [125,199,215]. This shows an increase in α for each component of the alloy compared with its separate deposition, which indicates that discharge of both metal ions is facilitated by codeposition.

It follows from the above discussion that, in consideration of the laws of the codischarge of ions under conditions of alloy electrodeposition, the displacement of the polarisation curves caused by the energy of formation of the alloy must be distinguished from the displacement due to a change in the nature and state of the cathode surface and in the electrochemical conditions of deposition. Whereas the former is always in the direction of more positive potentials (depolarisation), the direction of the latter may vary depending on which kinetic factors in the discharge predominate.

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MECHANISM OF CORROSION WITH LIMITED ACCESS OF ELECTROLYTE

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1. INTRODUCTION

Many engineering structures, items of chemical equipment, and instruments corrode most strongly, strange as it may seem, at those places to which access of the corrosive medium is difficult (flanged unions, shut-off equipment, hydraulic seals, constructional gaps and crevices, etc.).

This dangerous and widespread type of corrosion, which at first was most definitely and clearly exhibited in structural gaps and crevices, was called in the literature "crevice corrosion". Nowadays this term no longer reflects the variety of corrosion phenomena which arise as a result of restricted access of electrolyte to individual parts of fabrications and equipment. However, since this term has already taken deep root in the literature, we shall preserve it in the present review, but use it in a wider sense to cover, besides corrosion in crevices, selective linear dissolution of metals at the boundary of several phases, the corrosion of structures along the water-line, the development of pitting, etc.

Crevice corrosion plays an important part in the breakdown of structures in chemical equipment, diesel engines, atomic reactors, and instruments. Intense corrosion

develops not only in existing structural clearances and cracks, but also in those which arise during operation of the articles. Very important automatic devices, for example valves, often fail to operate owing to crevice corrosion, which entails serious consequences. The operation of devices having calibrated dispensing apertures breaks down in time, producing an excessive consumption of fuel, reagents, and occasionally even a failure in industrial processes.

Although great attention has been paid to crevice corrosion in several researches[1-17], the mechanism of the process has remained relatively little studied. This has impeded the development of rational methods of protection against corrosion, as well as the correct choice of materials for the manufacture of equipment and appliances.

Interest in crevice corrosion has revived recently, mainly owing to the requirements of industry, and these processes have begun to be widely studied, both in the Soviet Union and abroad.

In the explanation of crevice corrosion, the greatest currency has been attained by the ideas of differential aeration developed by Evans and Mears[2,4]. Further investigation has shown, however, that the mechanism of crevice corrosion cannot be reduced to differential aeration alone. Intensified crevice corrosion is often observed even in acid electrolytes, as well as in electrolytes which have been completely freed from oxygen. The processes which develop in crevices are in actual fact more complicated, and are governed by several factors. A far larger number of processes than had previously been assumed were found to occur by a mechanism of crevice corrosion. In particular, the corrosion of polyphase contacts in acid electrolytes[9-11], the pitting of stainless steels[12], and corrosion processes developing along the water-line[13,14] must be included in the above type of corrosion.

Electrochemical methods of investigating crevice corrosion[9,10,18] have been extremely fruitful, and have helped to establish several general laws and yield fresh results revealing the mechanism of crevice corrosion. They have shown convincingly that these phenomena are not associated with any special properties of the interface, but are caused by the change in the electrochemical properties of the metal at sites to which access of electrolyte is impeded.

It is now possible, on the basis of results obtained from a systematic study of a large number of metals[9,11,19,20], to elicit the most characteristic features of the process for most metals, and hence to formulate very general views on the mechanism of crevice corrosion.

The present paper reviews the most important results obtained in the study of crevice corrosion.

2. PECULIARITIES OF THE ELECTROCHEMICAL BEHAVIOUR OF METALS IN NARROW GAPS AND CREVICES

The specific character of electrochemical reactions occurring on metals in narrow gaps is due to difficulties in the access of corroding agents and passivators from the bulk of the electrolyte to the gap and the slow removal from it of the products of the electrochemical reactions[19,21,22]. Primarily it is the access of oxygen to the narrow gap that is greatly impeded, and this is responsible for several peculiarities in the course of anodic and cathodic reactions. The polarisation curves reproduced in Fig. 1 for iron in gaps show, for example, that in neutral electrolytes the rate of the anodic process is appreciably increased in the gap, while the cathodic process is retarded.

The accelerated ionisation of a metal in a gap is due to the fact that, as a result of the diminished concentration of oxygen in the crevice, anodic dissolution occurs at more negative potentials. The lower concentration of oxygen on the metal surface in the gap results in predominant formation of ferrous compounds, which possess no protective properties.

For the group of metals whose passive state is due to the presence of oxygen or other oxidant, obstacles to the access of these reagents to the crevice may so accelerate the anodic process that these metals begin to dissolve as active metals.

The diminished oxygen concentration in the gap has the opposite effect on the cathodic process: it makes both kinetic and diffusion stages of the process difficult. This is shown by the general displacement of the cathodic polarisation curves to more negative potentials (Fig. 1*b*) and the lower limiting diffusion current.

It is noteworthy that, after the gap has reached a certain width (0.25 mm) the limiting diffusion current becomes practically constant. The explanation is that the whole volume of electrolyte in such gaps is no longer mixed by convection, and transport of oxygen is effected only by diffusion.

The corrosion behaviour of metals in crevices and gaps can be predicted from the change in the kinetics of the electrochemical reactions. Metals which under normal conditions corrode with anodic control should be especially sensitive to crevice corrosion. Where, however, the rate of corrosion is governed by the kinetics of the cathodic reaction, corrosion in crevices will be slower than on a freely washed surface, since only the anodic reaction is accelerated, and in the given case does not govern the rate of spontaneous dissolution. It is assumed here, of course, that the duration of contact between metal and electrolyte is the same in the crevice and outside it. Actually, however, in atmospheric corrosion or even in corrosion under

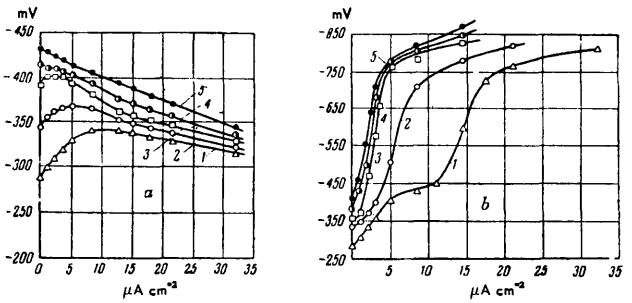

Fig. 1. Polarisation curves for iron in 0.5 *N* NaCl: *a*) anodic; *b*) cathodic: 1) in bulk; and in gaps of different width (in mm): 2) 1; 3) 0.5; 4) 0.35; 5) 0.25–0.05.

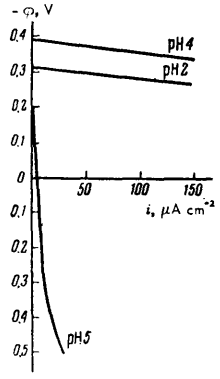

Fig.2. Potential dependence of rate of anodic ionisation of iron at various pH values.

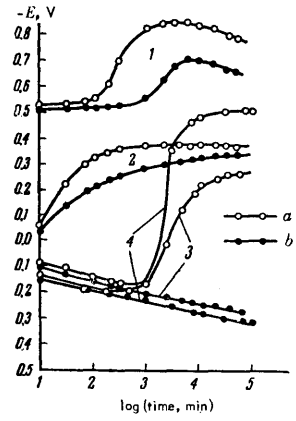

Fig.3. Time variation of steady-rate potentials of metals in 0.5 *N* NaCl: *a*) in a 0.05 mm crevice; *b*) on an open surface; for: 1) aluminium; 2) iron; 3) iron in (per litre) 70 mg Na_2SO_4 + + 30 mg NaCl + 250 mg $NaNO_2$; 4) stainless steel (13% Cr).

conditions of periodic wetting, electrolyte is retained considerably longer in the crevices, and for this reason corrosion is always more rapid in crevices than on an open surface.

The restricted supply of electrolyte to difficultly accessible sites results in a relatively rapid change in pH, which can be in either direction, as will be shown below. It is therefore necessary to consider how such changes influence the electrochemical behaviour of metals. As has been shown by one of us[23] and also by Iofa and Larin[10], an increase in pH in acid electrolytes (pH 1–4) accelerates the anodic ionisation of iron. In neutral electrolytes the opposite effect is produced, the anodic process being slowed down. These regularities are well illustrated by the polarisation curves in Fig. 2.

Study of the corrosion of many metals in gaps[19] confirms the theoretical prediction that crevice corrosion will depend on the nature of the controlling factor. Such metals as iron, zinc, and aluminium alloys of the Al–Zn–Mg–Cu (V95) and Al–Cu (D16) systems, in which corrosion is controlled by the rate of the cathodic reaction, corrode more slowly inside than outside crevices (with the same time of contact with the electrolyte). However, such alloys as Kh13, Kh17, AMTs, and AMG, which corrode with anodic control, are attacked more strongly in crevices than on a surface which is freely washed by the electrolyte.

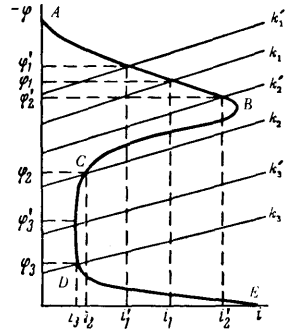

Fig.4. Potentiostatic curve representing behaviour of metals in crevices: *ABCDE*) anodic polarisation curve; k_1)–k_3) cathodic polarisation curves for open surface; k'_1)–k'_3) corresponding curves for surface in crevice; φ)–φ') steady-state electrode potentials.

3. CHANGE IN STEADY-STATE POTENTIALS AT SITES TO WHICH ACCESS OF ELECTROLYTE IS IMPEDED

The acceleration of the anodic ionisation of metal and retardation of cathodic depolarisation processes at sites to which access of electrolyte is impeded should result in the steady-state potential of metals being less noble at such positions. This has been confirmed by measurements on several metals in crevices[19] (Fig. 3), the potential in which may show a quite considerable shift to more negative values.

The change is especially great with stainless steels: with the steels Kh13 and Kh17, for example, the potential of the metal in a crevice is 0.55–0.60 V more negative than in bulk. The explanation is that, as a result of the insufficient supply of oxygen, the stainless steel passes from the passive into an active state, whereas iron, both in the bulk of the electrolyte and in a crevice, lies within the range of potentials characteristic of the active state, where there is no such strong dependence of potential on oxygen concentration.

In order to ascertain the possible consequences of the above changes in the kinetics of electrochemical reactions, it is useful to consider the potentiostatic curve for the anodic process (Fig. 4). Analysis of this curve shows that in principle crevice corrosion can develop in three ways: (1) when the steady-state potential of the metal is in the

active range, the negative shift in this potential occurring in a crevice, caused by the diminished efficiency of the cathodic process, should result in a lower rate of corrosion ($i_1 - i_1'$); and (2) and (3) when the steady-state potential of the metal is more positive than the potential of complete passivation, alloys may or may not be activated as a result of the hindrance to the cathodic process, depending on whether the steady-state potential of the metal is (2) close to the potential of complete passivation or (3) remote from the latter. In case (2) the negative shift in the steady-state potential in the crevice ($k_2 - k_2'$) results in activation of the metal and its intensified breakdown in the crevice ($i_2 - i_2'$); but in the last case ($k_3 - k_3'$) the passive state will not be disturbed ($i_3 - i_3'$).

It follows from the above that metals which are in a passive state should be especially sensitive to crevice corrosion, but the diminished efficiency of the cathodic process and the accelerated anodic process in crevices should not always produce activation of the alloy. If these changes in the kinetics of the electrochemical reactions do not bring the steady-state potential beyond the potential of complete passivation, activation will not occur. Although stainless and ordinary steels (the latter in the presence of inhibitors) are often activated in crevices the stable passive state of these metals can be preserved even in crevices provided that the chromium content of the alloy is sufficient or the solution contains sufficient inhibitor of oxidising type.

Hence it can be concluded that appliances which for engineering reasons contain gaps and crevices must be made of more highly alloyed steels, especially with higher contents of chromium and molybdenum.

4. CHANGE IN NATURE OF CORROSION MEDIUM IN GAPS

Strong crevice corrosion is to be expected in cases in which there is a clearly marked dependence of rate of corrosion on oxidant concentration, and especially in the presence of a critical concentration above which the alloy passes into the passive state. In this respect, the behaviour of iron in nitric acid is typical. Iron is passive in 8.6 N HNO_3. In crevices, however, where conditions for the continual renewal of the acid do not exist, and its concentration falls quite rapidly, corrosion is intensified (Fig. 5*a*).

Similar phenomena are observed when corrosion inhibitors, are used (Fig. 5*b*). Effective protection by an inhibitor depends on a constant supply of the latter to the metal surface[23]. Since such conditions do not obtain in crevices, the inhibitor concentration falls to critical values, which have been shown[23] to intensify instead of diminishing corrosion. Such a situation occurs in the presence not only of $NaNO_2$ and $K_2Cr_2O_7$ but also of Na_2HPO_4. In the last case strong corrosion is caused both by diminution in the phosphate concentration and also by inadequate supply of oxygen, in the absence of which phosphates are ineffective[24,28].

The dependence of intensity of corrosion on width of gap is interesting. Maximum corrosion is observed not with the minimum gap, to which access of reagent (HNO_3, $NaNO_2$) is most greatly impeded, but with some intermediate gaps. Such a relationship depends on the degree of breakdown of the passive state. The narrower the gap, the greater the proportion of the surface over which passivity has broken down, and corrosion becomes uniform

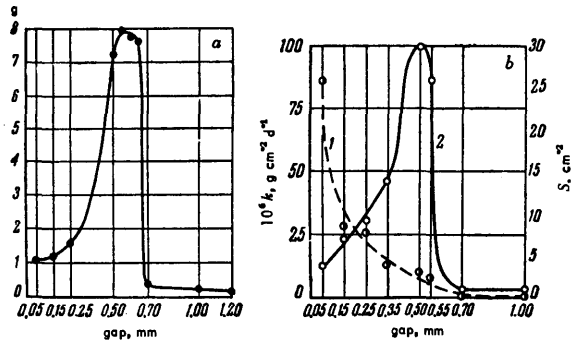

Fig.5. Dependence on width of gap of crevice corrosion of iron in oxidising agents: *a*) 8.6 N HNO_3; *b*) NaCl (30 mg litre^{-1}) + + Na_2SO_4 (70) + $NaNO_2$ (250): 1) corroded area; 2) intensity of corrosion.

in character. In intermediate gaps the concentration of oxidant is diminished to a smaller extent, and corrosion becomes local in character, penetrating to a relatively great depth.

In structures containing gaps and crevices, for example the cooling systems of diesel engines, which often break down, the total concentration of inhibitors must therefore be increased. This can be illustrated by results which we have obtained for the inhibitor concentrations required to ensure protection of a freely washed metal and of metal located in crevices (Table 1).

Apart from the above generalisations, the possibility of a change in character of the corrosion medium located in a gap must be taken into account. The small volume of the gap and the limited extent to which corrosion products diffuse away create conditions for more rapid saturation of the electrolyte by the corrosion products than in the bulk of the electrolyte. The formation of sparingly soluble hydroxides results in the rapid establishment of a definite pH in the gap, the value of which is controlled by the solubility product of the hydroxide. Thus saturation of a solution with $Fe(OH)_2$, $Al(OH)_3$, and $Mg(OH)_2$ respectively establishes pH values of 6.8–6.9,[25] 8.5, and 10.5.

With iron such a shift in pH is advantageous. With aluminium, however, the limit of the corrosion resistance of which in 0.5 NNaCl lies[26] within the pH range 6.5–8.0,

TABLE 1. Inhibitor concentrations required to protect steel in crevices (0.05 mm) and on open surface. Initial composition of electrolyte (mg litre^{-1}): 30 NaCl + + 70 Na_2SO_4.

Metal	$NaNO_2$, g litre^{-1}		$K_2Cr_2O_7$, g litre^{-1}		Na_2HPO_4, g litre^{-1}	
	open surface	crevice	open surface	crevice	open surface	crevice
Iron	0.1	2.0	0.07	1.20	3.60	30.0
Cast iron	0.95	11.5	0.08	1.00	—	—

displacement of the pH beyond these limits produces strong corrosion. For this reason the corrosion of aluminium is far greater in a gap (0.04 mm) than in bulk[20]. With decrease in the concentration of chloride ions, the pH limits of the corrosion stability of aluminium become wider[26], and therefore corrosion in crevices diminishes.

Hence it follows that the negative shift in the potential of aluminium in a gap is caused not only by the difficult access of oxygen but also by a change in the character of the corrosion medium. Moreover, as will be shown below, the greatest changes in corrosion medium in gaps result from the formation of macrocells of crevice–open surface type.

5. FORMATION OF MACROCELLS OF CREVICE–OPEN SURFACE TYPE

So far we have confined our discussion to the electrochemical and corrosion behaviour of metals in crevices alone. In reality, a metal in a crevice is always in contact with metal which is freely washed by electrolyte, and this circumstance substantially changes the character of the process[19]. Since, as was shown in Fig. 3, the potential of a metal in a crevice differs appreciably from its potential under free access of oxygen or other passivating agent, favourable conditions are created for the formation of macrocells, in which the metal in the gap constitutes the anode. The curves in Fig. 6, representing the time variation of the current arising between an electrode which is freely washed with electrolyte and an electrode located in a crevice, show that quite powerful cells can operate on various metals under such conditions.

A noteworthy feature is the presence of an induction period, during which the current from the cell is very small. With the steel Kh13, for example, a current was produced in 0.5 *N* NaCl after about 30 h, and with Kh17 after 28–30 d. This indicates that differential aeration cannot by itself initially secure the effective operation of such cells. Consequently there must be other factors producing a large current in the system. One of these we have already discussed, and this is the gradual loss of the passive state by the metal, owing to the restricted access of passivating agent. However, the change in the character of the corrosion medium in the crevice is no less important. Since the metal in the crevice has the more negative potential, it begins to act as anode in the corrosion cell, which immediately produces acidification of the corrosion medium in the crevice.

For example, our calculation for aluminium[20] decomposing water according to the equation $Al^{3+} + H_2O \rightleftharpoons Al(OH)^{2+} + H^+$ ($K_{AlOH^{2+}} = 1.4 \times 10^{-5}$) has shown that, with a current of 160 μA, the hydrogen-ion concentration in a gap (δ = 0.04 mm, v = 60 mm³) must be established at pH 3.5 after only 1 h. Experimental determinations give similar values (3.2–3.4).

With aluminium and stainless steels, such acidification of the medium causes further acceleration of anodic reactions in the crevice and produces stable operation of the macrocells, with ultimate breakdown of the metal in the crevice[20,27].

Differential aeration is thus merely the initial cause. The main attack on the metal in the crevice, however, is due to the appearance of active–passive macrocells, the functioning of which results in acidification of the corrosion medium in the crevice.

Hence the main requirement of material to be used for equipment containing structural gaps and crevices is relative insensitivity to change in pH.

In order to be able to predict the behaviour of metals in crevices, it was of interest to study the functioning of cells of crevice–open surface type, and determine the relation between the polarisation resistance and the ohmic resistance. Fig. 7 shows the corrosion diagram for the stainless steel Kh13, from which it follows that the existing view that ohmic control predominates in such systems is incorrect†.

Even in extremely fine gaps (0.05 mm) the system is practically completely polarised in 0.5 *N* NaCl. Owing to the facilitation of the anodic reaction in the crevice, the proportion of anodic control is small, and the working of

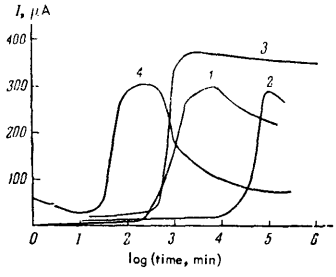

Fig. 6. Time variation of current flowing between two identical electrodes (of area 30 cm²), one being in a crevice and the other freely washed with electrolyte (0.5 *N* NaCl): 1) stainless steel Kh13 (13% Cr); 2) stainless steel Kh17 (17% Cr); 3) brass L62 (62% Cu); 4) aluminium.

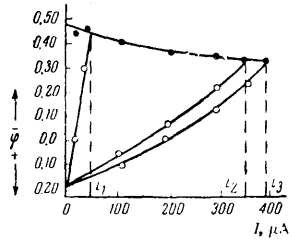

Fig. 7. Actual corrosion diagram for cell of type metal in gap (0.05 mm)–open surface of metal (stainless steel Kh13, 13% Cr) with 0.5 *N* NaCl as electrolyte and area of electrode in gap 30 cm². Ratio of areas: i_1) 1 : 1; i_2) 1 : 10; i_3) 1 : 15.

† An ohmic potential drop can be observed only in deep crevices.

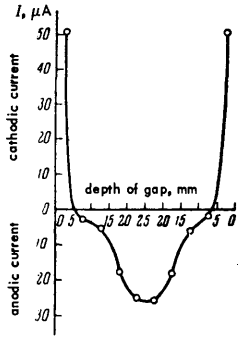

Fig.8. Distribution of current at different depths in crevice and polarity of different parts of metal in 0.5 *N* NaCl, with gap 0.1 mm wide and 25 mm deep.

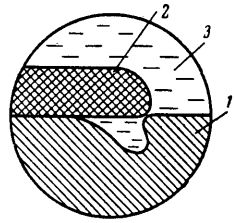

Fig.9. Corrosion structure produced in the corrosion of iron in contact with a dielectric in an acid; 1) metal; 2) paraffin wax; 3) acid.

such cells is controlled mainly by the rate of the cathodic reaction. With stainless steels of the Kh13 and Kh17 type, ohmic control proved to be so small that it could not be determined graphically. The proportion of anodic control was 4–20%, and that of cathodic control 80–96%. Since cathodic control predominates in the operation of such cells, as the diagrams show, the crevice corrosion of stainless steels and other passivated alloys should greatly depend on the cathode area, since the effectiveness of the cathodic process will increase with increase in the area of electrode which is freely washed by the electrolyte. Experiments which we have carried out under laboratory conditions[27], and by Ellis and La Que in natural seawater[8], have shown that the intensity of the crevice corrosion of stainless steels is directly proportional to the area of metal which is freely washed by electrolyte.

It must be noted that macrocells may arise within a crevice itself, owing to the difference between its edges and its centre in the rates of supply of depolarisers or corrosion medium and of removal of reaction products. This is clearly illustrated by the curve showing the distribution of current in a crevice (Fig. 8), which indicates that, as a result of the electrochemical inhomogeneity, the edges of the crevice act as cathodes, and the middle as anode[9].

6. SELECTIVE LINEAR DISSOLUTION AT PHASE BOUNDARY

The selective linear dissolution of iron at a three-phase boundary in acids occurs by the above mechanism, as our own work[9,11] and also that of Larin and Iofa[10] has shown. When in contact with a dielectric, iron and low-alloy steels break down in acids in a characteristic manner: a peculiar corrosion structure in the form of a deeply etched grove (Fig. 9) appears along the whole perimeter of the metal–dielectric boundary (the dielectric can be, for example, a blob of paraffin wax).

This interesting type of breakdown at one time attracted the attention of numerous investigators. Many hypotheses and guesses were made. Evans[2] assumed that the phenomenon was due to differential aeration; Kistyakovskii[29] and Mirlis[30] attributed it to the specific properties of dielectrics; and Tikhonov[31] supposed that portions of the surface on which bubbles of evolved hydrogen were resting became anodic zones.

The first experiments showed, however, that selective linear dissolution is observed even in electrolytes which have been completely freed from oxygen. Hence the phenomenon cannot be explained by differential aeration. Nor can the specific properties of dielectrics be used, since experiments have shown that the rate of selective linear dissolution along the perimeter is independent of the nature of the dielectric. Furthermore, such dissolution has been observed even on contact between two uniform metal surfaces.

Actually, the phenomenon is due to the formation of concentration cells. In the narrow gap along the perimeter between dielectric and metal, the pH of the electrolyte rises quite rapidly owing to reaction between metal and acid. Since access of fresh acid from the bulk of the electrolyte to the narrow gap is difficult, the difference in pH between crevice and bulk is maintained. It appeared that the rise in pH in the crevice should result in a diminished rate of corrosion. However, the situation is changed fundamentally by the existence of a contact between the metal in the crevice and the metal which is freely washed with electrolyte. As has been shown by one of us[23] and also by Larin and Iofa[10], increase in the pH of acid electrolytes makes the steady-state potential of a metal less noble and accelerates the anodic ionisation of the metal. It was found that, the greater the alkalinity of the electrolyte, the more easily does ionisation of metals occur.

$p H_2SO_4$ (*N*)	0.4	0.2	0.1	0.01	0.002
$\log i_a$	−3.90	−3.50	−2.70	−0.40	+0.1

This can be illustrated by the accompanying results obtained by Larin and Iofa[10] for the rate of dissolution of iron in sodium sulphate solution acidified with sulphuric acid, the electrolyte concentration being constant ($p + q$ = = 0.5 *N*). When the total concentration of sodium sulphate (q) and of sulphuric acid (p) was 0.5 *N*, the rate of anodic dissolution (i_a) at a potential of -0.250 V increased greatly with decrease in the concentration of sulphuric acid.

Similar results, indicating that the ionisation of iron becomes more rapid with increase in pH, were obtained by Kabanov and Leikis[32] and also by Bonhöffer and Heusler[33].

The former workers explained this interesting fact by the influence of hydroxide ions adsorbed on the surface, which facilitates ionisation of a metal. A relation between potential and pH such as that[23] illustrated in Fig. 10 provides conditions for the formation of a macrocell, with the metal in the gap as anode and the remainder of the surface as cathode.

The validity of the above mechanism can be demonstrated by the following striking experiments. If two identical iron sheets are taken, one of them is coated with a dielectric in such a way that a narrow crevice exists between metal and dielectric, and they are immersed in an electrolyte solution, an e.m.f. of 80–100 mV is established quite rapidly between the two electrodes, and a current (15–20 μA cm^{-2}) begins to flow. The anode in such a cell is the metal which forms the crevice with the dielectric.

Similar results can also be obtained with two identical electrodes which are connected to one another if the electrolyte (0.2 N H_2SO_4) around one of them is gradually made alkaline. A current flows in this case, too, its direction indicating that the metal in the more alkaline electrolyte is the anode (Fig. 11). This relation is maintained over a wide pH range, and only when this solution has become strongly alkaline (pH 12–13) does the metal in the more acid electrolyte become the anode. This is explained by the strong passivating effect of alkali, which makes the potential of the steel more positive.

A similar change in electrolyte pH takes place in the narrow gap between metal and dielectric, but in this case the increase in pH results from reaction of the acid with the metal, not from its neutralisation with alkali. The variation in pH in the crack is limited, since the anodic reaction products from the corrosion cell undergo hydrolysis and reacidify the electrolyte[20,27]. Ultimately a definite relation is established between the two processes, the pH usually reaching 2.5–3.5, *i.e.* the level which precisely favours the most efficient operation of the macrocell (see Figs. 2 and 11).

Interesting results have been obtained in a study of the functioning of similar concentration cells produced by change in the hydrogen-ion concentration (Table 2). When the concentration cell

$$Fe\,|\,(m+n)Na_2SO_4\,|\,mH_2SO_4+nNa_2SO_4\,|\,Fe$$

is on open circuit, the electrode in the acid electrolyte corrodes the more strongly. When, however, the electrodes are short-circuited, the situation is changed: corrosion of the electrode washed by the neutral electrolyte

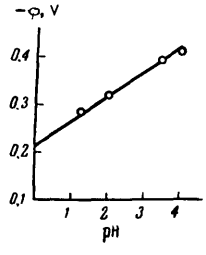

Fig. 10. Dependence of electrode potential of iron on pH.[23]

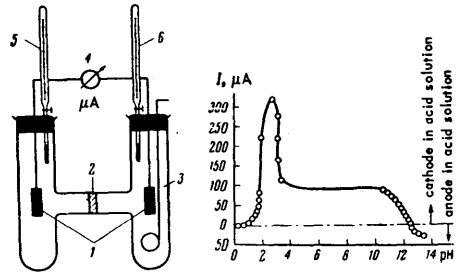

Fig. 11. Current flowing between two identical iron electrodes immersed in 0.2 N H_2SO_4 as function of pH of electrolyte around one of them (right-hand side). The left-hand side shows the apparatus for measuring such currents: 1) iron electrodes; 2) porous diaphragm; 3) stirrer; 4) microammeter; 5) and 6) microburettes.

TABLE 2. Rate of corrosion of iron electrodes (area 30 cm^2) of concentration cell in sulphate mixtures.

No.	Experimental conditions	I, μA	Rate of corrosion × 10^6, g m^{-2} d^{-1}		
			in absence of contact	in contact with	
				anode	cathode
1	0.2 N Na_2SO_4	—	5.23	—	—
2	0.2 N H_2SO_4	—	35.20	—	—
3	−Fe/0.2 N Na_2SO_4/0.2 N H_2SO_4/Fe, $S_a : S_c = 1 : 1$	200	—	30.26	33.09
4	−Fe/1 N Na_2SO_4/0.2 N H_2SO_4 + 0.8 N Na_2SO_4/Fe, $S_a : S_c = 1 : 5$	260	—	77.30	34.10

increases sharply‡. This is because the latter electrode becomes the anode, and anodic processes take place preferentially on it while the cathodic processes are in this case concentrated on the electrode in the acid electrolyte, the potential of which is kept at a more positive value by the high concentration of hydrogen ions and the slight polarisation. As a result of anodic polarisation, the rate of corrosion of the iron electrode in the neutral electrolyte is increased almost sixfold. The corrosion current of such a cell is 200 μA (Table 2). This occurs when the ohmic potential drop in the cell has been 90% of the initial potential difference§. If both internal and external resistances of the cell are reduced to a minimum, *i.e.* if the system is completely polarised, the current is increased

‡ Schikorr[34] and Liebreich[35] pointed out at one time that, if one sheet is placed in NaCl and another in HCl, and they are short-circuited, the sheet in the NaCl will corrode. In fact both electrodes corrode, and it is only under certain conditions, which will be discussed later, that corrosion of the electrode in the more alkaline electrolyte can be greater than that of the electrode in the acid electrolyte.

§ The high resistance is due to the diaphragm separating the anolyte from the catholyte.

by a factor of almost 18, and reaches about 3 mA. If, with the aim of decreasing the internal resistance of the cell, the concentration of the sulphate mixture is increased to 1 *N* and the area of the anode is diminished, which does occur in selective linear corrosion at a three-phase boundary, the rate of corrosion of the electrode in the neutral electrolyte (anode) is more than double the rate of corrosion of the cathode, *i. e.* the electrode in the acid solution.

7. CORROSION IN THE WATER-LINE ZONE

Very many structures are subject to strong attack in the region of the water-line (ships, gas-holders, cisterns, apparatus, etc.), corrosion being observed both directly at the water-line and below it (Fig. 12). At one time the mechanism of such processes was reduced to differential aeration[2]: *i. e.* it was supposed that, owing to the differential access of oxygen to portions of the metal situated along the water-line and below it, differential aeration couples were formed. The potential of the more aerated portion of the metal directly at the water-line became more noble, and the metal itself became the cathode; the portions below the water-line formed the anodes, and underwent corrosion.

However, strong corrosion along the water-line is often observed in acid medium, as well as in thoroughly stirred electrolytes, where differential aeration cannot play any important part. In order to explain such cases, the idea was put forward[2,14] of "surface competition", according to which products formed by reaction of the metal with the medium, which are usually protective in character, are deposited preferentially at the meniscus on the water–air interface, rather than at the water–metal interface.

Marshakov and Zanina[14] have recently made a detailed quantitative study of these phenomena, and established that most of them occurred by the mechanism of crevice corrosion discussed above. According to the views developed in this work[2,14], the meniscus at the metal–electrolyte–air boundary and the water-line is to be regarded as a narrow crevice, to which continuous access of electrolyte is greatly impeded. As a result, for example in acid media, the electrolyte near the meniscus becomes alkaline fairly rapidly, and the metal in this zone becomes more negative. A cell is formed in which the metal located directly at the water-line forms the anode, and undergoes intensified attack.

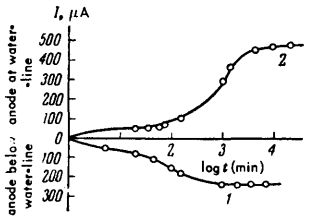

Fig. 12. Anodic zones arising at the water-line on iron[14]: 1) anodic processes concentrated below water-line in 0.1 M Na_2SO_4; 2) anodic processes concentrated at water-line in 0.1 M H_2SO_4. Perimeter along water-line 12 cm; area of electrode 50 cm^2.

It is interesting that a quantitative determination of the relation between ohmic and polarisation resistances has shown that, in spite of the narrow crevice formed by the meniscus, the ohmic resistance of the cell is low in this case, too. It has also been shown that the breakdown of steel in the water-line zone in inhibited media containing an incorrect quantity of the inhibitor likewise takes place by the mechanism of crevice corrosion. Very frequently cases of strong attack on structures along the water-line have been observed in media containing a concentration of inhibitor which, it would appear, should completely exclude corrosion. It has been found that these phenomena, too, are caused by the peculiarities of electrochemical behaviour of the metal at the meniscus, which forms a narrow crevice at the surface of the metal: as a result of inadequate access of inhibitor to this portion of the electrolyte, the concentration of inhibitor in it falls fairly rapidly, and the potential of the metal becomes more negative. It can be shown that under these conditions a quite powerful voltaic cell is formed, in which anodic processes are concentrated in the region of the meniscus, which also results in corrosion of the metal along the water-line. As these processes are not caused by any special properties of the water-line, but are due solely to a change in the concentration of inhibitor, dangerous corrosion at the water-line can be eliminated by using for such structures higher inhibitor concentrations than are usual, so that the concentration in the meniscus does not fall to dangerous levels.

8. PITTING

Stainless steels and other readily passivated alloys, usually distinguished by great resistance to oxidising media, are readily activated by halide ions. Activation takes place at a limited number of points, at which intense corrosion begins to develop rapidly, accompanied by the appearance of deep pits.

Such selective dissolution can be explained by variation, between different points on the surface, in the strength of bonding of the metal with the oxygen responsible for the passive state. At points where for some reason such bonding is weak, the oxygen is displaced by halide ions, and corrosion starts at these points. Once having begun, it must, in Kolotyrkin's opinion[36], accelerate, since halide ions, being the majority current carriers, begin to move towards these centres, increasing the concentration of activator.

Rozenfel'd and Danilov[12,37] have recently obtained results which enable the development of pitting to be explained on the basis of the above theoretical ideas concerning crevice corrosion. The new concept has been put forward, and confirmed experimentally, that pitting is to be regarded as the main form of crevice corrosion. Pits formed on the surface of stainless steels are mostly enclosed foci of corrosion, to which access of oxidant is impeded.

The diminished effectiveness of the cathodic process in a pit brings the steady-state potential of the latter beyond the potential of complete passivation, this being accompanied by loss of the passive state by the metal and acceleration of its anodic ionisation in the pit. The situation is still further complicated by the formation of powerful

macrocells, with the pits as anodes, as a result of the different conditions of access of the electrolyte to a pit, representing a relatively enclosed region, and to the rest of the surface, to which the electrolyte has free access. Owing to hydrolysis of the products of the anodic reaction, the functioning of such cells is accompanied by strong acidification of the medium in the pit with intensified attack on the metal in the latter. Thus from its very birth a pit represents a kind of crevice within which, because of insufficient access of passivator, favourable conditions are created for the rapid development of predominantly anodic processes.

It is obvious that, if pitting represents a special form of crevice corrosion, in which the peculiarities of the electrochemical behaviour of the metal are caused solely by a difference in access of corrosion medium and removal of corrosion products, as has been demonstrated, pitting should cease when identical access of electrolyte to the pits and to the rest of the surface is ensured. Experiments have supported this hypothesis. If the coating is removed from pits which form on a metal surface, and free access of electrolyte to them is thereby ensured, they stop growing. However, in closed pits, to which access of electrolyte, and hence of passivator, is difficult, corrosion continues to penetrate deep into the metal (Fig. 13, curves *1* and *2*).

Interesting results have been obtained also from a study of the number of points at which activation of the alloy with formation of a pit can occur. It is usually supposed that the surface of a stainless steel contains a limited number of points, governed by the structural peculiarities of the alloy, at which pitting can occur[38]. Experiments have shown, however, that this is not altogether the case: the number of pits increases continuously as previously formed pits are opened up (Fig. 14). This is explained by regarding each initially formed covered pit as a point protector, which greatly diminishes the probability of pits being formed at other points on the surface. If, however, the initially formed pits are uncovered, and their growth is thereby terminated, the protective effect disappears, and an ever increasing number of pits appear on the surface (Fig. 14, curves *2–4*). Consequently, doubt should be cast on the assumption that the metal surface contains some limited number of centres which are sensitive to pitting corrosion. In fact there are very many of them, and the formation of new pits is prevented only by the protective effect of previously formed pits.

The experimental work discussed above provides convincing support for the idea that pitting develops by the mechanism of crevice corrosion.

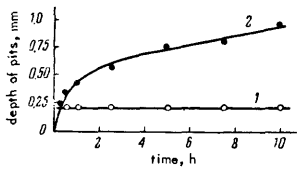

Fig.13. Penetration of corrosion into stainless steel 1Kh18N9T in 2% $NH_4Fe(SO_4)_2.12H_2O$ + + 3% NH_4Cl: 1) open pits; 2) closed pits.

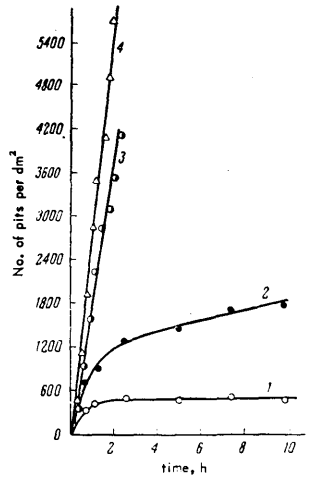

Fig.14. Pitting of stainless steel 1Kh18N9T in 2% $NH_4Fe(SO_4)_2.12H_2O$ + 3% NH_4Cl: 1) initial pits not uncovered; 2) pits uncovered after 0.5, 1, 2.5, 5, 7.5, and 10 h; 3) pits uncovered every 15 min; 4) as 3) but in electrolyte containing (per litre) 11.5 g $FeCl_3$ + + 25.5 g NaCl.

In conclusion it must be noted that the above phenomena obviously play a decisive role in the corrosion cracking of engineering structures, which usually begins with the appearance of extremely fine cracks in the metal, in which, owing to the insufficient access of electrolyte, anodic processes should develop preferentially.

It is remarkable that research on the above processes, which was initially cognitive in character and aimed at finding methods for slowing them down in order to prevent dangerous forms of breakdown in chemical equipment, has recently had an unexpected outcome in practice in an exactly opposite field — the chemical working of metals and alloys — which requires the rapid occurrence of electrochemical reactions. It has been found that the enhanced etchability of metals in narrow gaps and crevices can be very successfully utilised for the chemical milling, drilling, and cutting of especially hard and strong alloys which are difficult to machine.

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ADVANCES IN THE CHEMISTRY OF DIVINYLACETYLENE

S. A. Vartanyan

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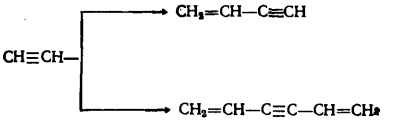
1. INTRODUCTION

Intense research into the chemistry of acetylene and its derivatives has led to the possibility of their preparation from many compounds which are nowadays used on an industrial scale as intermediate products. However, the great tendency of divinylacetylene and its homologues to polymerise and the danger of explosion of these polymers have until now retarded the development of the chemistry of divinylacetylene, despite the fact that divinylacetylene is very reactive, as a result of the presence of one triple and two double bonds, and constitutes an interesting raw material for organic synthesis. The numerous and various reactions of these compounds even at this stage suggest the possible ways of their utilisation in chemistry.

The advances in the chemistry of divinylacetylene have not been reviewed, except for Nazarov's article[1] which deals only with the mechanism of the hydration and cyclisation of dienynes. In the present review an attempt is made to collect, and as far as possible arrange in a systematic manner, the extensive data on this problem which are at present available.

2. SYNTHESIS OF DIVINYLACETYLENE AND ITS HOMOLOGUES

Mignonac and de Saint-Aunay[2] showed that, when acetylene is subjected to high frequency discharges at -60°, vinylacetylene and divinylacetylene (DVA) are formed. The authors explained the formation of DVA by postulating the addition of acetylene to vinylacetylene. The polymerisation of acetylene into vinylacetylene, DVA, and higher polymers under the action of concentrated aqueous solutions of cuprous chloride and ammonium chloride, discovered by Nieuwland and coworkers[3] in 1931, is of considerable importance for the synthesis of DVA:



Basically, the numerous studies on the synthesis of DVA are various modifications of Nieuwland's work[3]. Taking the available results as a whole, we can divide these syntheses into the following groups (bearing in mind the composition of the catalyst, the conditions, and the reaction medium): the use of Nieuwland's catalyst with modified concentrations of its various components[4-19]; replacement of ammonium chloride by other substances[6,7]; the use of anhydrous solvents[18-33], dispersing agents[24,25], carriers[26], high temperature[27-31], and acetylene under pressure[32].

In all cases DVA is formed together with vinylacetylene. By controlling the reaction conditions, preferential formation of either monovinylacetylene or DVA and higher polymers can be achieved. It has been established that increase of the reaction temperature and of the concentration of cuprous chloride lead to higher amounts of DVA. One of the patents of the Nippon Mining Company[33] indicates that acetylene can be polymerised to give a 100% yield of the trimer, *i.e.* DVA.

In the laboratory DVA can be prepared by the action of the magnesium bromide derivative of vinylacetylene or acetaldehyde followed by dehydration of the resulting methylvinylethynylmethanol[34]:

$$CH_3CHO + BrMgC{\equiv}C{-}CH{=}CH_2 \rightarrow CH_3{-}\underset{OH}{CH}{-}C{\equiv}C{-}CH{=}CH_2 \xrightarrow{-H_2O} CH_2{=}CH{-}C{\equiv}C{-}CH{=}CH_2 .$$

Divinylacetylene can also be obtained by the action of the di(magnesium bromide) derivative of acetylene on 1,2-dichloro-2-ethoxyethane followed by the splitting off of the ethoxy-group and the chlorine, by treatment with zinc, from the acetylene dichloride formed[35]:

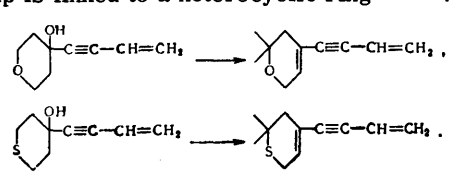
$$2\,CH_2{-}CHCl + BrMgC{\equiv}CMgBr \rightarrow CH_2{-}\underset{Cl}{CH}{-}C{\equiv}C{-}\underset{OC_2H_5}{CH}{-}CH_2{-}Cl \xrightarrow{-2\,OC_2H_5,\ -2\,Cl} CH_2{=}CH{-}C{\equiv}C{-}CH{=}CH_2 .$$

Iotsich[36] obtained 1,1,6,6-tetrachlorodivinylacetylene by the action of zinc on the acetate of the acetylene glycol derived from chloral:

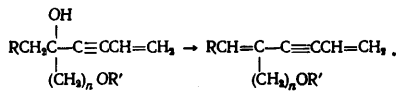
$$CCl_3{-}\underset{OCOCH_3}{CH}{-}C{\equiv}C{-}\underset{OCOCH_3}{CH}{-}CCl_3 \rightarrow CCl_2{=}CH{-}C{\equiv}C{-}CH{=}CCl_2 .$$

Apart from the first representative of the divinylacetylene hydrocarbons, DVA itself, which is mainly obtained by polymerisation of acetylene, substituted divinylacetylenes are prepared by dehydration of vinylacetylene alcohols and acetylene glycols. As a result of Nazarov's work, vinylacetylene alcohols are readily available. Dehydration of these alcohols yields a series of divinylacetylenes containing one substituted vinyl group[37]. It has been established[37-47] that tertiary vinylacetylene alcohols readily split off water on heating with practically all the dehydrating agents — sulphuric, phosphoric, acetic, formic, *p*-toluenesulphonic acids, acetic anhydride, etc.

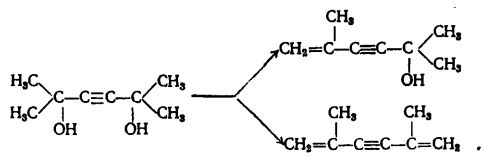
In practice the most convenient method of dehydrating vinylethynylmethanols is heating with 50–60% sulphuric acid; the yield of the corresponding dienyne then amounts to 70–90%. This method of dehydration makes it possible to synthesise also divinylacetylene compounds in which one vinyl group is linked to a heterocyclic ring[40,41,47]:



Dehydration of α- and β-alkoxyvinylacetylene alcohols takes place similarly[43-46]:



When acetylene 1,4-glycols are shaken with 20–40% sulphuric acid and heated on a water-bath, two molecules of water are split off and divinylacetylene hydrocarbons are obtained[48-56]. This is one of the convenient methods of synthesising dienynes. Dupont[52] established that dehydration of acetylene glycols takes place in two stages with the formation of substituted vinylacetylene alcohols which then lose yet another molecule of water and the corresponding dienyne is obtained:



Phosphoric acid (60%) has also been used for this purpose[50]. Other workers have also used potassium hydrogen sulphate as dehydrating agent[57-60]. Zalkind and Shuvalov[60] used sodium instead of potassium hydrogen sulphate at 150°. Marvel[49] and Babayan[61] showed that acetylene glycols are smoothly dehydrated under the action of *p*-toluenesulphonic acid at 140–150°, the yields of dienynes reaching 90%. Petrov and Korlik[62] established that oxalic acid can also be employed for the dehydration of acetylene glycols. Krestinskii and Summ[63] showed that tetraethylbutyne-1,4-diol is dehydrated on being shaken with formic acid, the expected dienyne being formed in almost theoretical yield.

However, it must be noted that on dehydration of vinylacetylene alcohols and acetylene glycols it is not always possible to isolate the expected dienyne, because under the reaction conditions side-reactions occur. Sometimes under the dehydration conditions the dienynes undergo direct cyclohydration with the formation of cyclic ketones[49]. The Meyer–Schuster rearrangement[64] also frequently occurs, and also cyclohydration of the glycols into the corresponding furandiones[65]. Recently a continuous method of synthesising divinylacetylene hydrocarbons, by vapour-phase dehydration of vinylacetylene alcohols over aluminium oxide at 150–400°, has been developed. An industrial process for the manufacture of vinylisopropenylacetylene has been proposed[66].

3. POLYMERISATION OF DIVINYLACETYLENE

DVA is a colourless liquid which rapidly becomes yellow on standing without a stabiliser; b.p. 85°/680 mm; n_D^{20} = = 1.5047; d_4^{20} = 0.7759.[67] On being kept in air, it absorbs oxygen, forming peroxy-compounds, and polymerises into a brittle polymer which readily explodes as a result of mechanical action — impact, friction, or heating. On heating the polymerisation of DVA is greatly accelerated. To prevent the formation of the peroxy-compounds, experiments on the polymerisation of DVA must be carried out either in the presence of a stabiliser or in an atmosphere of an inert gas[68]. The first stage of the polymerisation then yields a viscous product of an amber colour which gradually thickens and is converted into a brittle infusible and non-explosive mass[69]. The latter does not dissolve in organic solvents, is very stable to acids, alkalis, chlorine,

and bromine, and has therefore been suggested as a coating for various surfaces[69,70]. Morozov[71] suggested that the surface of electrodes used in the electrolysis of alkali metal chlorides should be impregnated with the DVA polymer. In the presence of anti-oxidants (pyrogallol, hydroquinone, α-naphthol, etc.) DVA can be kept in a closed vessel for about a year. On longer storage, it becomes yellow and polymerises. According to the literature, the intermediate liquid DVA polymers possess the properties of rapidly drying oils[71-83]. Their solutions in butyl acetate and other solvents yield satisfactory stable films on drying. Copolymers of propene and pentene with DVA and vinylacetylene, obtained in the presence of catalysts, can be used for coating metallic and glass surfaces. On heating with sulphur dichloride, DVA is converted into a resin or a liquid mass which is also suitable for coating metals[84].

Products with the properties of drying oils are also obtained on reaction of DVA with hydrogen polysulphide. The liquid polymers thus formed are recommended for the preparation of films, varnishes, and for various coatings[85]. Other workers have used hydrogen sulphide and sulphur; the reaction was carried out under pressure in the presence of dibutylamine, pyridine, sodium hydroxide, and ammonia[86].

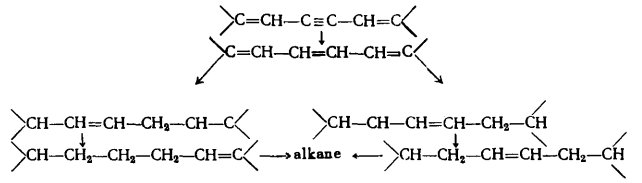
Drying oils are also obtained when chlorine is allowed to act upon the liquid polymers of DVA.[87] Despite the fact that the films and varnishes obtained from DVA age rapidly and become brittle, they have been recommended for use as drying oils[71], adhesives for rubber and metals[87], additives to Diesel fuel[88] and lubricating oils[89], and also as plasticisers for natural rubber[90,91]. In the presence of sodium naphthenate and gelatin DVA polymerises into a rubberlike product[92]. On heating for 10 h at 90°, divinylacetylene is converted into a mixture of dimer and trimer. Carothers distilled the dimer under a high vacuum and established that its molecular weight is 156, which corresponds to the formula $C_{12}H_{12}$. On bromination the dimers yield octa- and deca-bromides, on hydrogenation they absorb twelve hydrogen atoms, and on oxidation they are converted into *trans*-cyclobutane-1,2-dicarboxylic acid[93]. According to Carothers, the dimer has the structure of *trans*-1,2-di(vinylethynyl)cyclobutane and the trimer of di(vinylethynylcyclobutyl)acetylene.

Substitution of the hydrogen atoms of divinylacetylene by various radicals (aliphatic, alicyclic) enhances its stability to polymerisation. The substitution of the terminal hydrogen atoms has a particularly great inhibiting effect on polymerisation. Tetra-substituted divinylacetylenes polymerise either very slowly or not at all. As a result of the conjugated system of two double and one triple bond, they exhibit high elevation of molecular refraction (up to 5–6 units).

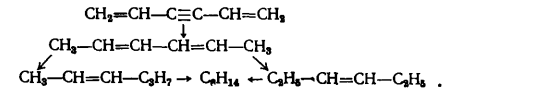
Like divinylacetylene itself, mono- or di-substituted divinylacetylenes thicken on standing, are converted into a viscous jelly, and finally into a solid mass of orange colour. On the walls of the vessel they form characteristic solid peroxy-compounds which explode on impact or friction. In a thin layer divinylacetylene polymerises in the course of several hours into a solid film.

4. HYDROGENATION

Blomquist and Marvel[48] were the first to show that divinylacetylene hydrocarbons are completely hydrogenated in the presence of a platinum catalyst with the formation of the corresponding saturated hydrocarbons. It was then established that, depending on the nature of the catalyst and on the method of its preparation, the hydrogenation of DVA and also its homologues takes place more vigorously when they are freshly distilled. In the presence of a palladium catalyst the hydrogenation stops after absorption of six hydrogen atoms (instead of the expected eight), whereas in the presence of a platinum catalyst eight hydrogen atoms are absorbed and the corresponding saturated hydrocarbon is formed. Some workers[48,53] believe that the first molecule of hydrogen adds to the triple bond with the formation of a 1,3,5-triene; the second hydrogen molecule can add on to the 2- or 4-positions. In the presence of a platinum catalyst a saturated hydrocarbon is then formed and in the presence of palladium an olefin:

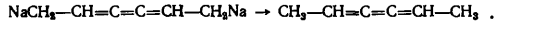


The hydrogenation of divinylacetylene itself was studied by many workers[94-99]. According to the data of Komada[96], the product is hex-3-ene and according to Katake[97] hex-2-ene. Isagulyants and coworkers[99] studied the hydrogenation of DVA in solution in ethanol, acetic acid, and xylene at the normal pressure or under a high pressure of hydrogen in the presence of a nickel catalyst. They established that the product is hexa-2,4-diene, whose formation is explained by the double addition of hydrogen to the 1- and 4-positions; further hydrogenation of hexa-2,4-diene yields hex-2-ene, hex-3-ene, and also hexane:



Klebanskii[94], who used palladium deposited on barium sulphate as the catalyst, established that the hydrogenation of DVA stops at the triene stage. Other workers showed that in the presence of platinum or nickel catalysts dienynes are hydrogenated to the corresponding saturated hydrocarbons. According to these workers, the reaction proceeds *via* the formation of 1,3-diene.

When divinylacetylene is reduced with sodium amalgam[94], hydrogen adds on to the 1- and 6-positions with the formation of 2,3,4-hexatriene:

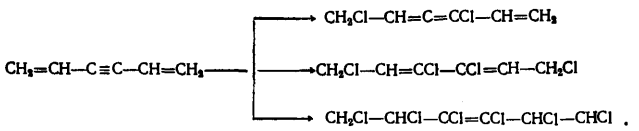


Klebanskii explains the addition of metal atoms to the 1- and 6-positions by the fact that the acetylene bond in the divinylacetylene molecule increases the electron density at the terminal atoms. When divinylacetylene is hydrogenated under a pressure of 10 atm in the presence of catalysts, the product is a mixture of hexenes, hexadienes, and hexatrienes, which can be used as rapidly drying oils[82]. Drying oils are also obtained on hydropolymerisation of DVA.[82]

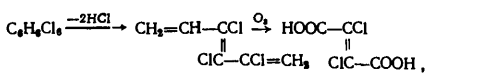
5. ADDITION OF HALOGENS

Chlorination of divinylacetylene[100] yielded di- and tetra-chlorides and also crystalline hexachlorohex-3-ene which

has the odour of camphor and is formed as a result of successive addition of chlorine to divinylacetylene to the 1- and 4-positions:

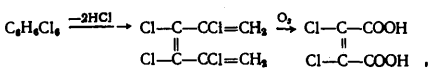


Two isomers of 1,2,3,4,5,6-hexachlorohex-3-ene were isolated. The structure of these hexachlorides was established by splitting off two molecules of hydrogen chloride in both isomers and subsequent ozonolysis [101]. Ozonolysis of the tetrachlorohexatriene obtained from the isomer with m.p. 59° yielded dichlorofumaric acid. On this basis, a *trans*-configuration was assigned to the initial hexachlorohex-3-ene:



m.p. 59°.

Ozonolysis of the tetrachlorohexatriene obtained from the isomer with m.p. 91° gave dichloromaleic acid, and therefore the isomer has the *cis*-configuration:

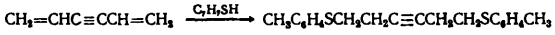


m.p. 91°.

Bromine adds to divinylacetylene similarly, with the formation of two stereoisomeric hexabromides [3,34,102]. The bromination takes place so smoothly that some workers use this reaction for the identification of divinylacetylene [3,34].

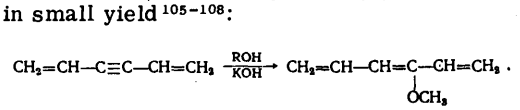
6. ADDITION OF THIOPHENOLS

Thiocresol adds on to divinylacetylene at the 1- and 2-positions (with respect to the vinyl groups) with the formation of 1,6-di-*p*-tolylthiohex-3-yne, which on oxidation with permanganate in acetone yields β-*p*-tolylsulphonylpropionic acid [103]:



7. ADDITION OF ALCOHOLS

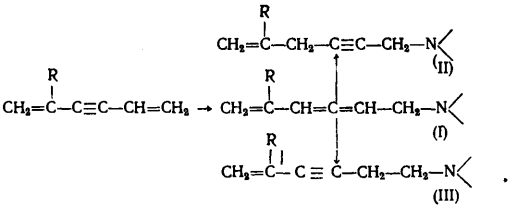
Dry methanol does not add to DVA under the action of a mercury catalyst [104,105], but there are data which suggest that the addition occurs at the 1- and 4-positions on heating in the presence of sodium alkoxide [106-108]. When divinylacetylene is boiled in methanol in the presence of sodium alkoxide for 40-60 h, 3-methoxyhexa-1,3,5-triene is formed in small yield [105-108]:



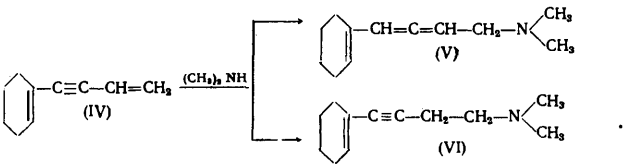
According to Klebanskii's data, under these conditions ethanol adds to divinylacetylene at the 1- and 6-positions [107,108]. Klebanskii also achieved the addition of ethanol to divinylacetylene on boiling in the presence of alkali and showed that under these conditions the addition also takes place at the 1- and 6-positions. It is possible that the mode of addition of alcohols depends on the alkyl radical. Methanol adds on to the 1- and 4- and ethanol to the 1- and 6-positions [106,107].

8. ADDITION OF AMINES

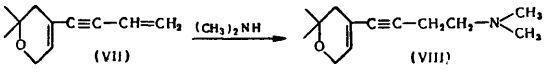
In order to synthesise amines derived from vinylacetylene, Vartanyan and Badanyan [109] studied the addition of amines to divinylacetylene hydrocarbons. They found that, when a mixture of an aqueous solution of dimethylamine and dienyne is heated in a sealed tube at 95-100° (40 h), one molecule of the amine adds to the dienyne at the 1- and 4-positions, so that the amino-group becomes attached to the terminal carbon atom of the substituted vinyl group; the resulting trienynylamine (I) undergoes two types of isomerisation under the reaction conditions, amines derived from allylacetylene (II) and vinylacetylene (III) being formed:



The structure of the amines was demonstrated by oxidation, hydrogenation, and synthesis. A study has also been made of the addition of amines to divinylacetylene systems in which one vinyl group is present in an alicyclic or tetrahydropyran ring. It was shown that under these conditions dimethylamine adds to Δ^1-cyclohexenylvinylacetylene (IV), also with the formation of amines derived from allene (V) and acetylene (VI):

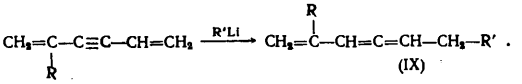


The addition of dimethylamine to the dienyne (VII) takes place similarly, but in this case only the expected aminoalkylacetylene (VIII) [110] is obtained in good yield:



9. ADDITION OF LITHIUM ALKYLS

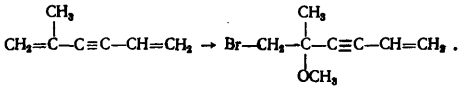
It has been established that lithium alkyls add on to divinylacetylene hydrocarbons at the 1- and 4-positions on the side of the unsubstituted vinyl group [111], triene hydrocarbons (IX) being obtained:



10. ADDITION OF ROX, $ROCH_2Cl$, and $C_6H_5N_2Cl$

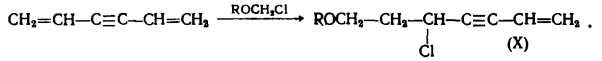
Petrov and coworkers [112] showed that electrophilic addition of methyl hypobromite to divinylacetylene, isopropenylvinylacetylene, and 3-methylhepta-2,6-dien-4-yne takes place at the double bond, and in the case of the last two dienynes only in the substituted vinyl group. Thus in this

case electrophilic addition of methyl hypobromite occurs in accordance with the electronic configuration of these dienes:

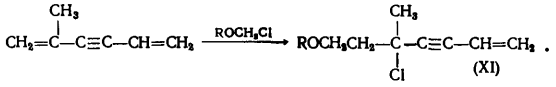


Ethyl hypochlorite[113] adds to DVA in a similar manner to methyl hypobromite[112].

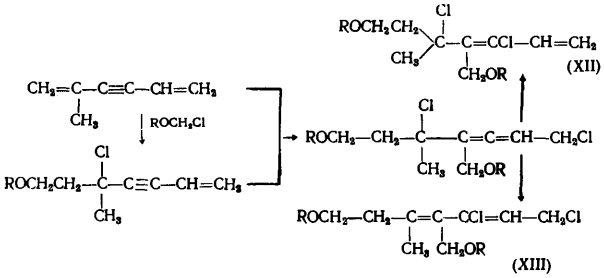
In the presence of zinc chloride in ethereal solution α-chloroalkyl ethers add on to DVA[114,115] at the 1,2-position with the formation of vinylacetylene chlorides (X):



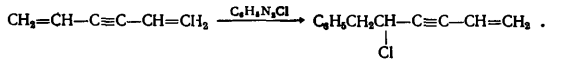
It has been established that in the case of isopropenylvinylacetylene the chloroalkyl ether adds to the double bond with the higher electron density and the monochloride (XI) is formed:



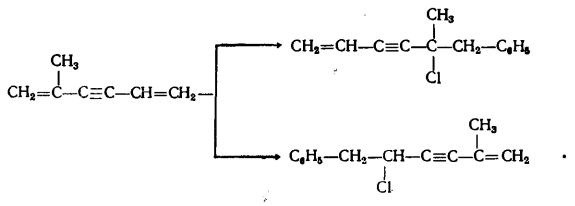
With isobutenylvinylacetylene and Δ^1-cyclohexenylvinylacetylene the reaction proceeds similarly. Apparently the addition of the second molecule of α-chloroalkyl ether to the vinylethynyl radical of the newly formed monochloride takes place at the 1- and 4-positions, yielding an allene dichloride, which under the conditions of the experiment isomerises into two dichlorides (XII) and (XIII). It has been established that the dichloride (XII) can isomerise to the dichloride (XIII) both under the conditions of the reaction and on standing without a catalyst. The reverse isomerisation is not observed. These dichlorides are obtained both when one molecule of α-chloroalkyl ether reacts with the monochloride (XI) and by direct interaction of two molecules of the α-chloroalkyl ether with isopropenylvinylacetylene:



On chloroarylation divinylacetylene combines with the aryl group and chlorine, which add mainly to the vinyl group:

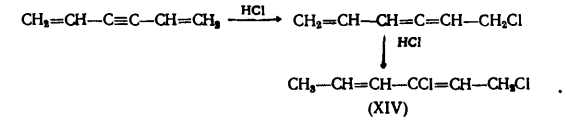


In the case of isopropenylvinylacetylene reaction takes place both in the vinyl and the isopropenyl groups with the formation of a mixture of the corresponding chlorides, but in each case the phenyl group adds on only to the terminal carbon atom of the double bond[116]:

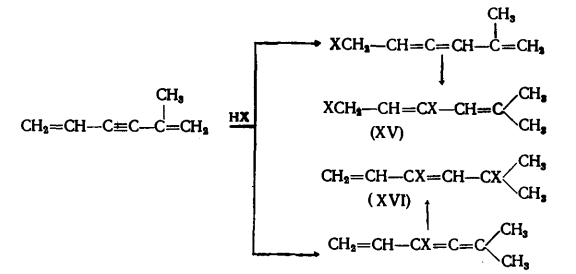


11. ADDITION OF HYDROGEN HALIDES

In the presence of cuprous chloride and ammonium chloride in aqueous solution hydrogen chloride adds on to DVA at the 1- and 4-positions, this being followed by the addition of a second molecule of hydrogen chloride at the other end of the molecule, also at the 1- and 4-positions, so that the final product is 1,3-dichlorohexa-2,4-diene (XIV):[117,118]

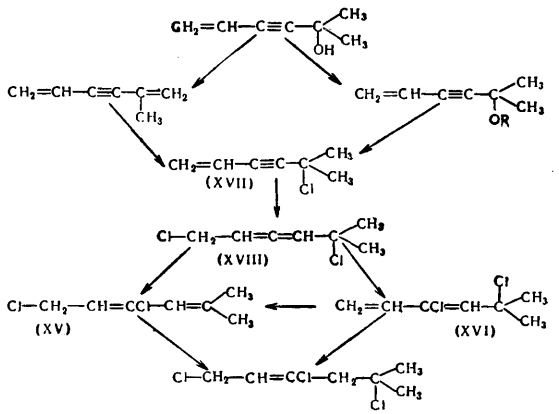


Hydrogen chloride undergoes successive addition to vinylisopropenylacetylene at the 1- and 4-positions, yielding a mixture of 1,3-diene dichlorides (XV) and (XVI).[119,120] Similar results were obtained in the hydrochlorination of dimethylvinylethynylmethanol and chlorodimethylvinylethynylmethane[121]. However, the dichlorides were not isolated in the pure state. The addition of hydrogen bromide takes place similarly[122]:

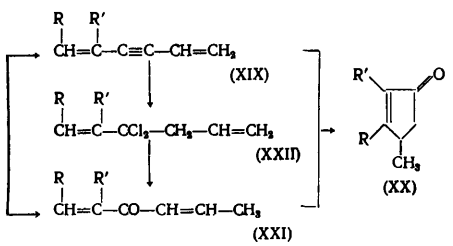


As a result of the further investigation of the hydrochlorination of these compounds, Nazarov and coworkers concluded that only the primary dichloride (XV) is formed[123]. However, subsequent detailed study of the hydrochlorination of isopropenylvinylacetylene, dimethylvinylethynylmethanol, and chlorodimethylvinylethynylmethane established that Nazarov's initial hypothesis was correct and that hydrochlorination indeed results in the formation of two isomeric dichlorides (XV) and (XVI).[124] But in all cases the addition of the first molecule of hydrogen chloride involves the formation of the monochloride (XVII) in the first stage, *i.e.* the first molecule of hydrogen chloride adds on at the 1- and 2-positions of the substituted vinyl group of isopropenylvinylacetylene. The monochloride (XVII) is also formed when hydrogen chloride reacts with dimethylvinylethynylmethanol or its methyl ether, the hydroxy- or the methoxy-group being replaced by chlorine. Thus the above findings show that in both cases the monochloride (XVII) forms in the first stage of the reaction. It appears that subsequently hydrogen chloride adds on to the vinylethynyl group of the monochloride at the 1- and 4-positions, with the formation of the intermediate allene chloride (XVIII), which under the conditions of the experiment isomerises to the dichlorides (XV) and (XVI). It was shown that under the given experimental conditions the dichloride (XVI) isomerises to the dichloride (XV), but the reverse isomerisation has not been observed. Hence it can be supposed that the dichloride (XVI) can be obtained both by the isomerisation of the dichloride (XVIII) and by the addition of a second molecule of hydrogen chloride to chlorodimethylvinylethynylmethane at the 3- and 4-positions. The dichloride (XV) can form as a result of the isomerisation of either one of the dichlorides (XVI) and (XVIII).

It has been shown that in the presence of the cuprous chloride and ammonium chloride catalysts the dichloride (XV) predominates in the mixture of (XV) and (XVI), whereas in the presence of aluminium chloride the main product is (XVI). Both dichlorides undergo hydrochlorination at 60° with the formation of the same trichloride:



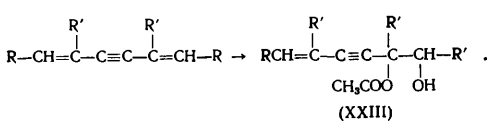
Nazarov and Yanbikov[125] established that disubstituted divinylacetylenes (XIX) undergo cyclohydration under the action of concentrated hydrochloric acid at 60–70° with the formation of the corresponding cyclopentenones (XX), and they were unable to isolate any products of the addition of hydrogen chloride to dienynes. They concluded that either direct hydration of the triple bond of these compounds takes place with the formation of the corresponding divinylketone (XXI), which under the conditions of the experiment cyclises into the cyclopentenone, or the divinylketone forms as a result of the addition of two molecules of hydrogen chloride to the triple bond of the dienyne followed by hydrolysis of the resulting dichloride (XXII):



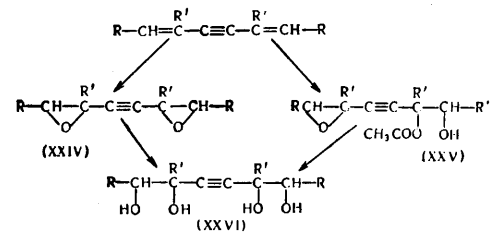
It is interesting to note that hydrochlorination of alkyl-β-methoxyethylvinylethynylmethanol and the product of its dehydration, alkoxydienyne, yields isomeric dichlorides, while the expected cyclopentenones are not formed[126].

12. OXIDATION OF DIVINYLACETYLENE HYDROCARBONS

Malenok and coworkers studied the oxidation of divinylacetylene hydrocarbons with acetyl hydroperoxide[127–129]. They showed that, when the oxidising agent reacts with the dienyne hydrocarbons in stoichiometric proportions, the vinylacetylene alcohol-acetate (XXIII) is formed:

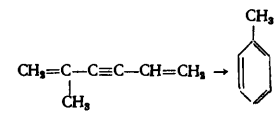


When two molecules of acetyl hydroperoxide are used per molecule of dienyne, the main products are the corresponding acetylene dioxides (XXXIV), together with a small amount of the monoxide (XXV). The latter is a product of the reaction between the newly formed dioxide and acetic acid. Acetylenic tetrols (XXVI) were obtained by the hydrolysis of the oxides (XXIV) and (XXV):

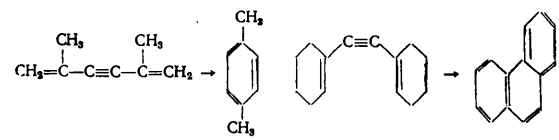


13. CYCLISATION

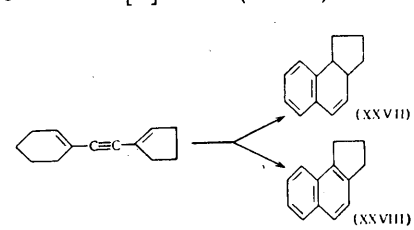
The aromatisation of divinylacetylene hydrocarbons and their partially hydrogenated derivatives has been studied in detail by Kotlyarevskii and coworkers[130–136]. Some data on this problem also exist in the patent literature[137–139]. The aromatisation of divinylacetylene hydrocarbons is of interest from the point of view of synthesis, because it makes possible the controlled synthesis of aromatic hydrocarbons with a prescribed structure which depends on that of the initial dienynes. Kotlyarevskii and Zanina[131] showed that, when isopropenylvinylacetylene (or products of its partial hydrogenation, up to the absorption of three molecules of hydrogen) is passed over the catalyst $MgO–CrO_3–Al_2O_3$ (2 : 18 : 80) at high temperatures, toluene is obtained in good yield:



Benzene was prepared similarly from DVA in 15–20% yields. Under these conditions diisopropenylacetylene cyclises into *p*-xylene[133], while di-Δ^1-cyclohexenylacetylene yields phenanthrene in 70% yield[134]:

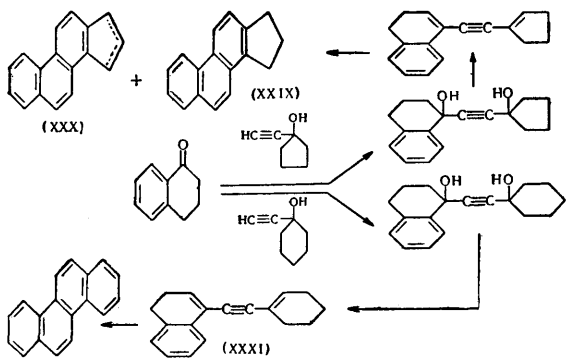


The method has also been used for the synthesis of tri- and tetra-cyclic condensed aromatic hydrocarbons, from which condensed hydrocarbons with a five-membered ring can be obtained by catalytic dehydrocyclisation. When Δ^1-cyclohexenyl-Δ^1-cyclopentenylacetylene is passed over a magnesium oxide-promoted aluminium oxide–chromium oxide catalyst, dehydrocyclisation takes place with the formation of 2,3,10,11-tetrahydro-1*H*-benz[*e*]indene (XXVII) and 2,3-dihydro-1*H*-benz[*e*]indene (XXVIII):



These compounds are of considerable interest for the preparation of polycyclic compounds with interesting carbon skeletons.

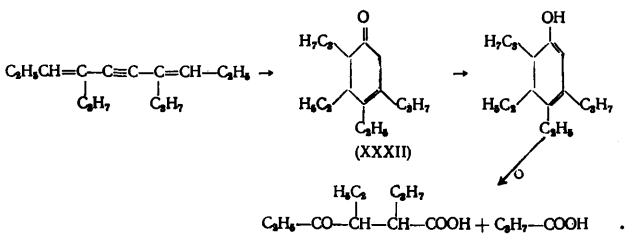
15,16-Dihydro-17*H*-cyclopenta[*a*]phenanthrene (XXIX) and 17*H*-cyclopenta[*a*]phenanthrene (XXX) were synthesised from α-tetralone and 1-ethynylcyclopentan-1-ol as follows[136]:



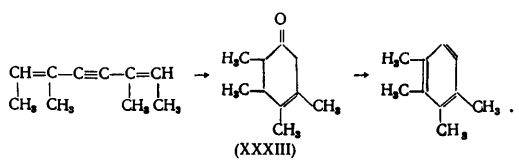
By a similar procedure chrysene was obtained from α-tetralone and 1-ethynylcyclohexan-1-ol *via* the dienyne (XXXI).

14. CYCLOHYDRATION

By the action of sulphuric acid on 4,7-dipropyldeca-3,7--dien-5-yne in acetic acid solution, Blomquist and Marvel[48] obtained 2,5-dipropyl-3,4-diethylcyclohexenone (XXXII) whose structure was proved by ozonolysis. The authors assumed that before ozonolysis the ketone (XXXII) undergoes enolisation as a result of which β-ethyl-γ-oxo-α--propylhexanoic and propionic acids are formed:

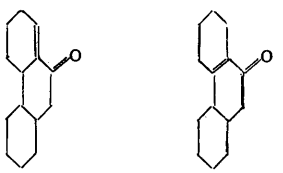


Later Mitchell and Marvel[50] established that diisopropenylacetylene cannot undergo the above cyclisation, but 3,6-dimethylocta-2,6-dien-4-yne does so with the formation of the cyclic ketone (XXXIII). The structure of the latter was demonstrated by Clemmensen reduction, followed by dehydrogenation to 1,2,3,4-tetramethylbenzene:

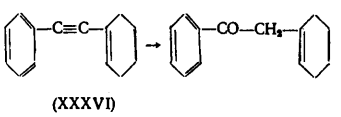


Marvel and coworkers[49] subjected di-Δ¹-cyclohexenylacetylene to cyclohydration under the action of formic acid and isolated two cyclic ketones — liquid and crystalline. The structure of the liquid isomer, dodecahydro-9-phenanthrone, was demonstrated by hydrogenation to perhydrophenanthrene; the authors were unable to establish the structure of the crystalline isomer.

Linstead and coworkers[140] also state that cyclisation of di-Δ¹-cyclohexenylacetylene results in the formation of two isomeric ketones. However, unlike Marvel, they found that both ketones are crystalline (m.p. 39° and 88°). Spectroscopic analysis showed that they are αβ-unsaturated ketones, in agreement with the results of other workers[141,142]. It was shown that dehydrogenation in the presence of platinum yields phenanthrene while the hydrogenation of each isomer separately results in the formation of the same 9-oxotetrahydrophenanthrene. On the basis of these findings, the authors attributed the structure (XXXIV) to the low-melting isomer and the structure (XXXV) to the high-melting isomer.

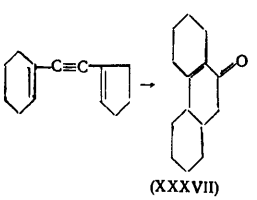


It has been established that when one of the double bonds of the dienyne is present in a six-membered ring, as in compound (XXXVI), the dienyne is still hydrated to the corresponding unsaturated ketone, but the latter can no longer undergo cyclisation into the expected cyclic ketone[56,59]:

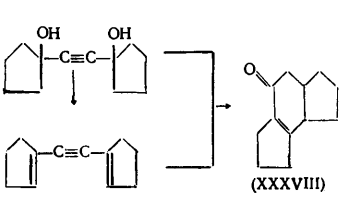


It has also been shown that dienynes with at least one hydrogen atom at the terminal carbon atom undergo cyclisation.

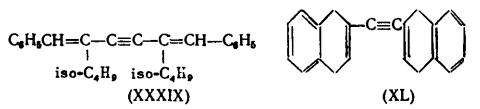
Under the action of formic acid Δ¹-cyclohexenyl-Δ¹--cyclopentenylacetylene cyclises into the tricyclic ketone (XXVII):[143]



When zinc amalgam and hydrochloric acid act upon di-Δ¹--cyclopentenylacetylene and the corresponding acetylene glycol, the latter compounds cyclise into the corresponding cyclohexane derivatives (XXXVIII):[56]

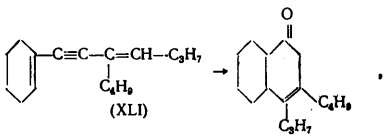


It is interesting that, when both double bonds of the diene are conjugated with an aromatic ring [compounds (XXXIX) and (XL)], cyclohydration does not occur.

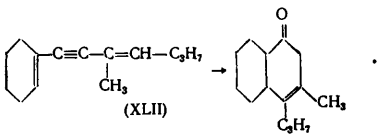


(XXXIX) (XL)

It has been established that the dienynes (XLI) and (XLII) are also capable of cyclising under the action of formic acid[54]:

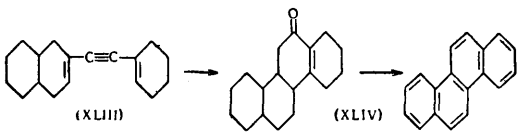


(XLI)



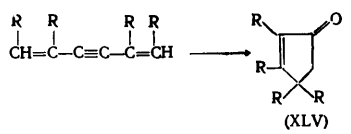
(XLII)

Cyclohydration of the dienyne (XLIII) yields the tetracyclic ketone (XLIV). The latter was subjected to Clemmensen reduction and dehydrogenated with platinum, the final product being chrysene[144]:



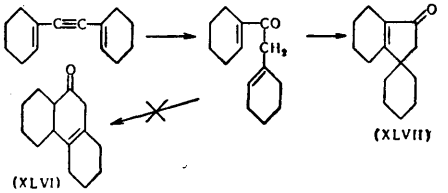
(XLIII) (XLIV)

The investigations of Marvel and coworkers, who studied the cyclohydration of a number of substituted dienynes quoted above, undoubtedly yielded erroneous results. This follows from the work of Nazarov and coworkers[1] on numerous and various examples. The latter showed that cyclohydration of dienynes and the cyclisation of divinyl ketones results in the exclusive formation of substituted cyclopentenones† and not cyclohexenones as stated by Marvel and coworkers. In particular, on the example of 3,6-dimethylocta-2,6-dien-4-yne Nazarov and Verkholetova[145] showed that not only asymmetric dienynes but also symmetric tetrasubstituted dienynes undergo cyclisation into the corresponding cyclopentenones (XLV) under these conditions:



(XLV)

Independently of one another, Nazarov and coworkers[146,147], Bogert and coworkers[148], and Linstead and Doering[149] showed that di-Δ^1-cyclohexylacetylene also readily undergoes cyclohydration under the above conditions with the formation not of the so-called "Marvel's ketone" *i.e.* a ketone with a phenanthrene skeleton (XLVI) but a ketone with a spiran structure (XLVII):



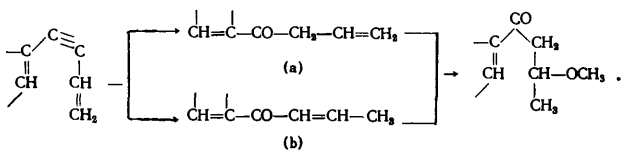
(XLVI) (XLVII)

The final proof that this ketone is not a phenanthrene derivative is provided by the detailed investigations of Linstead and coworkers[149].

15. SYNTHESIS OF β-ALKOXYKETONES BY HYDRATION OF DIVINYLACETYLENE HYDROCARBONS IN AQUEOUS SOLUTIONS OF ALCOHOLS

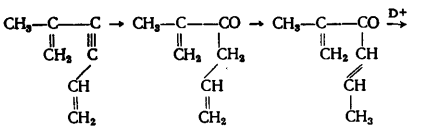
In contrast to acetylene derivatives, until recently the hydration of divinylacetylene hydrocarbons was not investigated at all. Nazarov and coworkers were the first to develop a very simple and effective method of hydrating divinylacetylene hydrocarbons[1]. The latter, on heating in aqueous solutions of methanol in the presence of small amounts of sulphuric acid and mercuric sulphate, are smoothly hydrated to the corresponding dienones, which under the conditions of the experiment combine with one molecule of methanol with the formation of β-methoxyketones, in most cases in high yields.

In all cases the addition of water takes place in such a way that the oxygen is directed to the acetylene carbon atom which is combined with the substituted vinyl radical:

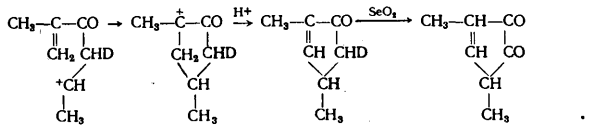


(a) (b)

In order to establish the structure of the dienones, (a) and (b), Nazarov and coworkers[151] prepared deutero-2,4-dimethyl-Δ^2-cyclopenten-1-one by the action of deuterated phosphoric acid on the dienone obtained on hydration of 2-methylhexa-1,5-dien-3-yne. By oxidation with selenium dioxide, they convincingly showed that the resulting 2,4-dimethyl-Δ^2-cyclopentene-1,5-dione does not contain deuterium. It follows therefore that deuterium was present in deutero-2,4-dimethyl-Δ^2-cyclopenten-1-one at carbon atom 5, *i.e.* in the methylene group adjacent to the carbonyl. This constitutes proof that 2-methylhexa-1,4-dien-3-one (B) cyclises and not the isomeric 2-methylhexa-1,5-dien-3-one (A).

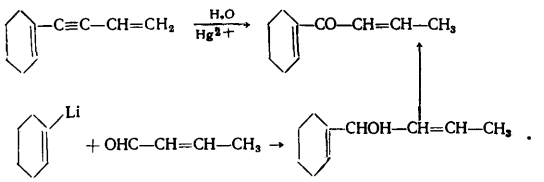


(A) (B)



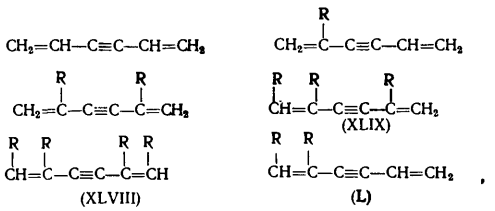
† Nazarov's review[1] deals with this problem. We may note that at present even in the non-Soviet literature this reaction is known as the Nazarov[150] and not Marvel cyclisation.

Quite recently Nazarov and Zaretskaya [152] demonstrated experimentally that hydration of Δ^1-cyclohexenylvinylacetylene yields not allyl Δ^1-cyclohexenyl ketone but Δ^1-cyclohexenylpropenyl ketone. The latter was also synthesised in a different way and proved to be identical with the product obtained on hydration of Δ^1-cyclohexenylvinylacetylene:



Thus the work of Nazarov shows that hydration of divinylacetylene hydrocarbons results in the formation not of allyl vinyl ketones but of the isomeric divinyl ketones.

According to the ease of hydration, Nazarov [1] divides dienyne into three groups:



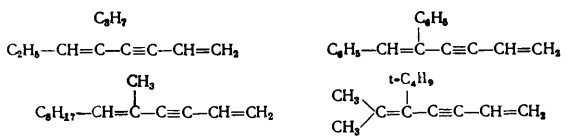
where R = alkyl, aryl, or a cyclic residue.

Group (XLVIII): symmetrical dienynes, in particular divinylacetylene itself; the compounds are hydrated at the lowest rate (in the course of 15–20 h) with good yields of β-methoxy-ketones.

Group (L): asymmetric disubstituted dienynes; they are hydrated very readily, usually in 1–2 h, with the formation mainly of β-methoxy-ketones in quantitative yields.

Group (XLIX): asymmetric mono- and tri-substituted dienynes; as regards ease of hydration they occupy an intermediate position.

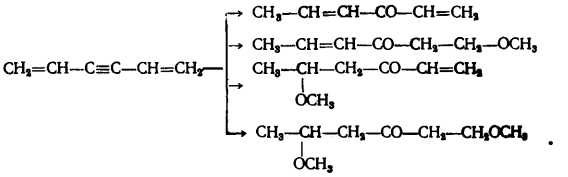
Thus the rate of hydration of dienynes to a great extent depends on the disposition of the substituents in them, an asymmetric disposition favouring hydration, which is undoubtedly associated with the increased polarity of the molecule. It has been shown that the dipole moments of asymmetric dienynes are higher [153]. This explains the fact that hydration of asymmetric dienynes occurs in only one way, the elements of water adding to the triple bond in such a way that the oxygen always becomes attached to the carbon atom which is linked to the substituted vinyl group. It has also been established that not only the disposition but the nature of the substituents has a very great effect. Introduction into the dienyne molecule of aromatic and large aliphatic residues slows down the reaction, which is probably due to steric hindrance. Thus, for example, the following dienynes are difficult to hydrate despite their asymmetric structure [154-157]:



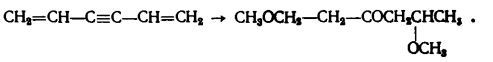
Thus divinylacetylene itself and symmetrically substituted dienynes are the most difficult to hydrate. Introduction of one and particularly two substituents into one of the vinyl radicals of the dienyne (asymmetric substitution) greatly accelerates the reaction. As the size of the substituent increases, the rate of hydration again falls.

Attempts to hydrate divinylacetylene to allyl vinyl ketone under the conditions of Kucherov's reaction have been unsuccessful [77]. Only a very small quantity of a product was isolated, to which the structure of the allyl vinyl ketone was attributed without proof. As shown later by Nazarov and Zaretskaya [104,157], the physical constants of this substance are similar to those of the products of the further hydration of allyl vinyl ketone, namely 2-methyltetrahydro-4-pyrone.

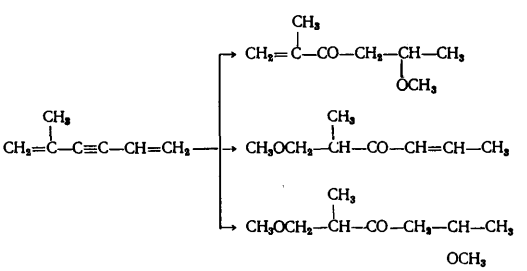
The hydration of divinylacetylene was achieved for the first time [158] in 1942 in aqueous methanol in the presence of sulphuric acid and mercuric sulphate. The resulting dienone (propenyl vinyl ketone) was converted under the conditions of the experiment into a mixture of 1,5-dimethoxyhexan-3-one and unsaturated methoxy-ketones by the addition of one or two molecules of methanol:



This reaction was studied in detail, the concentration of methanol, the reaction time, the temperature, and the composition of the catalyst being varied. As a result, it was found [159] that addition of sulphuric acid is not only unnecessary but that it actually enhances resinification. In the presence of mercuric sulphate without sulphuric acid in 90–95% aqueous alcohol divinylacetylene is hydrated in the course of 20 h, a good yield of 1,5-dimethoxyhexan-3-one being obtained:

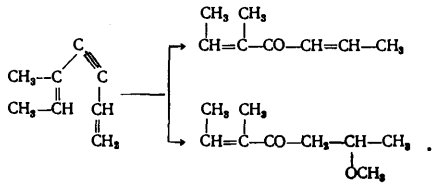


Isopropenylvinylacetylene, which is obtained in good yield on dehydration of dimethylvinylethynylmethanol, is relatively readily hydrated under similar conditions [104,105]. The hydration of this dienyne in aqueous methanol yields isopropenyl propenyl ketone, which under the conditions of the experiment combines with one or two molecules of the alcohol with the formation of the corresponding β-methoxy--ketones:

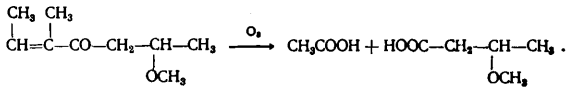


Like the above dienynes, 5-methylhepta-1,5-dien-3-yne very readily undergoes total hydration in aqueous solutions of methanol at 60–65° in the presence of small amounts

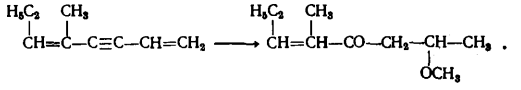
of sulphuric acid and mercuric sulphate, the products being the methoxy-ketone and a mixture of two isomeric dienones [37] which differ sharply from each other in their physical constants. When methanol is split off from the methoxy-ketone, only the high-boiling isomer of the dienone is formed. On hydrogenation both isomers yield only one saturated ketone:



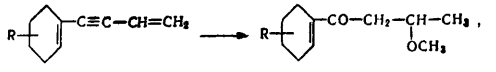
On more prolonged heating of the dienyne under the above conditions, the main product is 2-methoxy-5-methylhex-5-en-4-one. On ozonolysis of the methoxy-ketone, acetic and β-methoxybutyric acids are formed in good yields:



In another investigation Nazarov and Zaretskaya [160] studied the hydration of 5-methylocta-1,5-dien-3-yne, obtained by dehydration of methylpropylvinylethynylmethanol. As in the previous case, the dienyne hydrates readily with the formation of 5-methylocta-2,5-dien-4-one, which like the previously investigated 5-methylhepta-2,5-dien-5-one, is apparently obtained as a mixture of two geometrical isomers. In the presence of mercuric sulphate methanol readily adds to the propenyl radical of each isomer, the corresponding methoxy-ketones being formed:

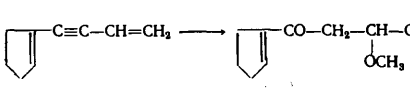


In the hydration of alicyclic dienynes, as in the hydration of other asymmetrically substituted divinylacetylene hydrocarbons, the addition of water to the triple bond is such that the oxygen always combines with the carbon atom linked to the substituted vinyl radical. Addition of water which would result in the formation of tetrahydrobenzyl vinyl ketone is not observed [161].

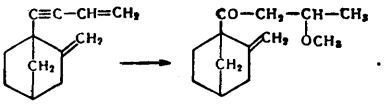


where R = H, CH_3.

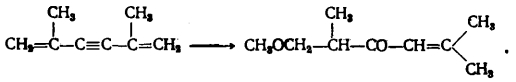
Under the above conditions the hydration terminates after 2 h. On further heating of the reaction mixture for 5–6 h almost the entire dienone is converted into Δ^1-cyclohexenyl β-methoxypropyl ketone. Ozonolysis of the latter gives β-methoxypropionic and adipic acids. On heating in 80–85% methanol under the above conditions Δ^1-cyclopentenylvinylacetylene is readily hydrated with the formation of two isomeric dienones (liquid and crystalline) which under the conditions of the experiment readily combine with methanol yielding the same Δ^1-cyclopentenyl β-methoxypropyl ketone. The latter on distillation with *p*-toluenesulphonic acid splits off methanol, yielding only the crystalline Δ^1-cyclopentenyl propenyl ketone [162].



The corresponding β-methoxy-ketone is also formed [163] on hydration of vinylethynylcamphene (obtained on dehydration of vinylethynylborneol):

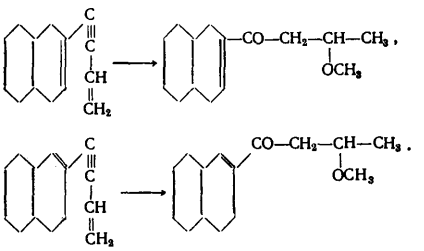


On heating in 90% methanol in the presence of sulphuric acid and mercuric sulphate, 2,5-dimethylhexa-1,5-dien-3-yne (obtained by dehydration of tetramethylbutynediol) is hydrated to 2,5-dimethylhexa-1,5-diene-3-one [164]. The hydration of this symmetrically substituted dienyne takes place with much greater difficulty than that of asymmetric dienynes.



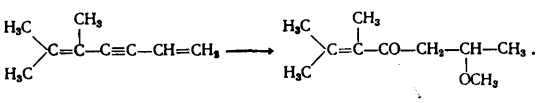
Under the conditions of the hydration reaction, methanol adds to the isopropenyl group of 2,5-dimethylhexa-2,5-dien-3-one with the formation of 2,5-dimethyl-1-methoxyhex-4-en-3-one. The latter on distillation in the presence of *p*-toluenesulphonic acid splits off methanol with the reformation of the initial dienone. Hydration of 3,6-dimethylocta-2,6-diene-4-yne yields 3,6-dimethylocta-2,5-dien-4-one which is incapable of combining with methanol [145].

When 2-vinylethynyl-2-decanol is heated with 50% sulphuric acid for 5 h at 55–60°, it is dehydrated yielding a mixture of 2-vinylethynyl-$\Delta^{1(2)}$-octalin and 2-vinylethynyl-$\Delta^{2(3)}$-octalin. When this mixture is hydrated in 95° methanol in the presence of sulphuric acid and mercuric sulphate, the product (70% yield) is a mixture of liquid and crystalline propenyl $\Delta^{1(2)}$-octahydro-2-naphthyl ketones [165,166], which can be readily separated by freezing out. On more prolonged hydration of the dienynes (more than 5 h), the principal, or even the only products, are methoxy-ketones which on vacuum distillation in the presence of *p*-toluenesulphonic acid split off methanol, and the initial dienones are reformed; hydrogenation yields the corresponding saturated methoxy-ketone:

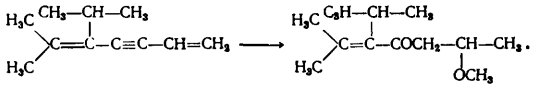


The structure of the unsaturated methoxy-ketones has been demonstrated by ozonolysis.

On heating in aqueous methanol under the above conditions, 5,6-dimethylhepta-1,5-dien-3-yne is quantitatively hydrated with the formation of 5,6-dimethylhepta-2,5-dien-4-one, which under the conditions of the experiment combines with one molecule of methanol and is converted into 5,6-dimethyl-2-methoxyhept-5-en-4-one [167]. On vacuum distillation in the presence of *p*-toluenesulphonic acid, the latter splits off methanol and reforms the initial dienone:

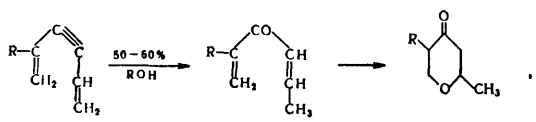


5-Isopropyl-6-methylhepta-1,5-dien-3-yne, obtained by dehydration of diisopropylvinylethynylmethanol on heating in aqueous methanol in the presence of sulphuric acid and mercuric sulphate, is readily hydrated to the corresponding dienone, whose propenyl group combines with methanol and 2-methoxy-5-isopropyl-6-methylhept-5-en-4-one is formed[168]. On careful heating of the latter in the presence of 0.5% of *p*-toluenesulphonic acid (15 min at 120–130°), methanol is split off with the reformation of the initial dienone (in high yield), which on more prolonged heating cyclises into the corresponding pentenone:



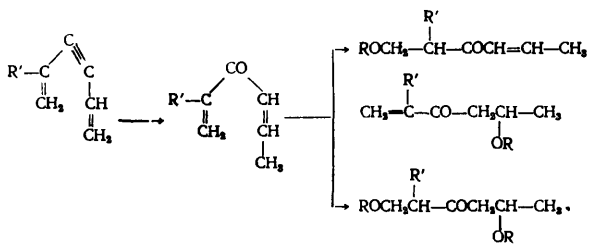
The above findings show that hydration of divinylacetylene hydrocarbons in aqueous methanol may be regarded as the simplest and most convenient method of the synthesis of β-methoxy-ketones. It has been established[169] that dienones can be hydrated in different alcohols, which makes it possible to obtain a wide variety of β-alkoxy-ketones. Depending on the conditions, this reaction results in the formation of β-alkoxy-ketones or tetrahydro-γ-pyrones. In order to obtain β-alkoxy-ketones, water is gradually added to the heated mixture of the alcohol and the dienyne, while tetrahydro-γ-pyrones are obtained when the dienyne is added dropwise to the water–alcohol mixture. The ease and the time required for the hydration of dienynes depend also on the nature of the alcohol used, the rate of hydration being lower when the latter has a branched structure and a high molecular weight.

When divinylacetylene and isopropenylvinylacetylene are heated in 50–60% aqueous ethanol or methanol in the presence of mercuric sulphate and sulphuric acid, the corresponding tetrahydro-γ-pyrones are obtained in 50% yield:

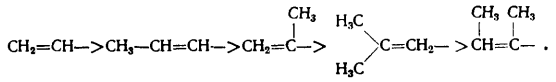


where R = H, CH_3.

In the hydration of divinylacetylene in 80–95% alcohol, considerable amounts of a mixture of alkoxy-ketones, whose structure has been elucidated by ozonolysis, are formed in addition to the pyrone:



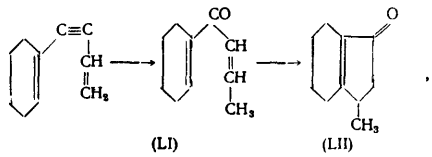
It has been shown that a disubstituted vinyl group is incapable of combining with alcohols (even methanol), the propenyl group combines with alcohols more readily than the isopropenyl group, and that the unsubstituted vinyl group undergoes the addition reaction most readily[170]. With respect to the rate of addition of the alcohols (and also amines and other compounds) to αβ-unsaturated ketones, vinyl radicals can be arranged in the following series[169]:



It must be noted that, when the hydration of dienynes is carried out in solution in isopropenyl alcohol, the only reaction product is the monoalkoxy-ketone (R = iso-C_3H_7), *i.e.* isopropenyl alcohol proves to be quite incapable of adding to the isopropenyl group of isopropenyl propenyl ketone.

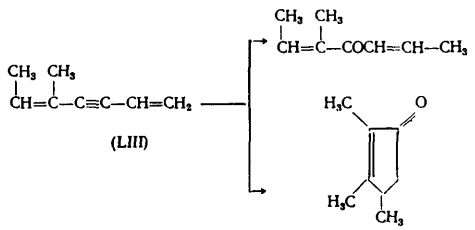
Disubstituted asymmetric enyne hydrocarbons are also readily hydrated in aqueous alcoholic solutions in the presence of mercuric sulphate and sulphuric acid. The hydration is completed in 3–4 h but here instead of the expected β-alkoxy-ketones the hydration products are only the corresponding unsaturated ketones. Prolonged experiments (24 h) have shown that, instead of combining with the alcohols, these unsaturated ketones cyclise into the corresponding cyclopentenones.

On heating in 95–98% ethanol or butanol for 3–5 h in the presence of mercuric sulphate, Δ^1-cyclohexenylvinylacetylene is completely hydrated to the corresponding unsaturated ketone (LI) [169] which in more prolonged experiments partly cyclises into 1-methyl-4,5,6,7-tetrahydroinden-3-one (LII):



(LI) (LII)

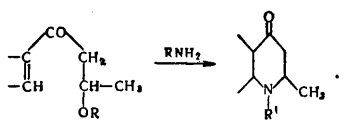
hydration of 3-methylhepta-2,6-dien-4-yne (LIII) in ethanol or butanol for 20–26 h yields a mixture of 3-methylhepta-2,5-dien-4-one and 2,3,4-trimethylcyclopent-2-en-1-one:



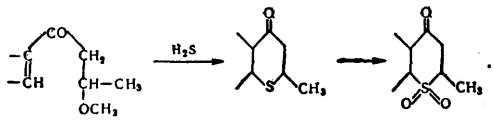
(LIII)

The above data show that, under the above conditions of the hydration reaction, ethanol and butanol are incapable of adding to the αβ-unsaturated ketones described. This makes it possible to hydrate asymmetric disubstituted enyne hydrocarbons to the corresponding αβ-unsaturated ketones, which could not be achieved when these dienynes were hydrated in methanol, since under the conditions of the hydration reaction the unsaturated ketones formed are capable of combining with one molecule of methanol to yield β-methoxy-ketones. The divinyl ketones thus obtained have become readily available and are now the simplest unsubstituted starting materials for the synthesis of a wide variety of carbocyclic and heterocyclic ketones of the tetrahydropyran, thiopyran, and piperidine series. For example, when aqueous ammonia or aqueous solutions of primary amines are allowed to act upon β-alkoxy-ketones,

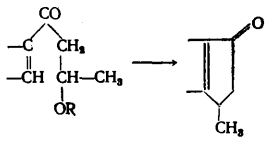
the corresponding γ-piperidones are obtained in high yields[171]:



The action of hydrogen sulphide on allyl vinyl ketones in alcoholic solutions of sodium acetate or amines results in the formation, in high yields, of a wide variety of tetrahydro-γ-thiopyrones[172] which are readily oxidised by potassium permanganate in acetone solution to the corresponding sulphones:



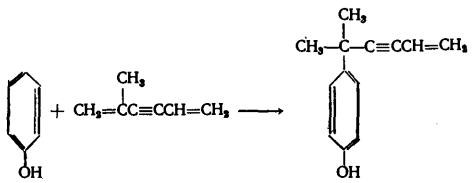
When treated with phosphoric acid (and also other acids), allyl vinyl ketones are extremely readily and often quantitatively cyclised into the corresponding cyclopentenones[1]:



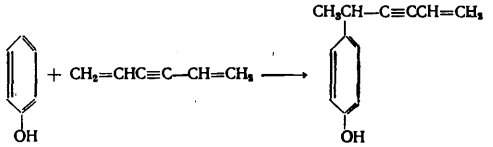
The discovery of very simple methods for the preparation of heterocyclic ketones (γ-piperidones and tetrahydrothiopyrones), which were previously difficult to obtain, has led to the recent extensive development of the search for and synthesis of new physiologically active and medicinal substances. In particular, it has been possible to synthesise a whole series of new ethers of the piperidine series with exceptionally high analgesic activity, several times greater than that of morphine and other natural products.

16. ALKYLATION AND CYCLOALKYLATION

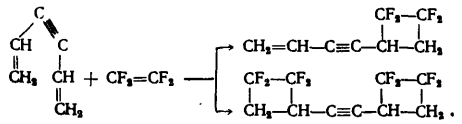
It has been shown that, when isopropenylvinylacetylene is heated with phenol in the presence of phosphoric acid, p-substituted phenols are obtained[173,174]:



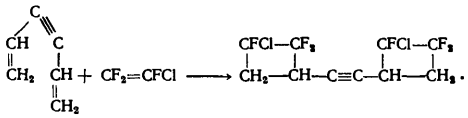
The alkylation of phenol with DVA takes place similarly[175]:



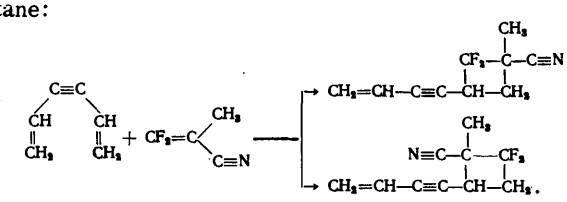
Quite recently it has been shown[176] that heating of DVA with tetrafluoroethylene in the presence of 0.1 g of N-phenyl-β-naphthylamine for 11 h at 125° results in the formation of bis-(2,2,3,3-tetrafluorocyclobutyl)acetylene and 1,1,2,2-tetrafluoro-3-vinylethynylcyclobutane. The products of addition to the triple bond were not obtained.



Chlorotrifluoroethylene condenses with DVA in 6.5 h at 150° with the formation of bis-(2-chloro-2,3,3-trifluorocyclobutyl)acetylene:

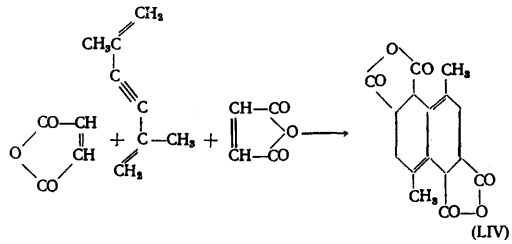


Condensation of DVA with $\beta\beta$-difluoro-α-methacrylonitrile yields an adduct consisting of a mixture of the isomers of 1-vinylethynyl-2,2-difluoro-3-methyl-3-cyanocyclobutane and 1-vinylethynyl-3,3-difluoro-2-methyl-2-cyanocyclobutane:



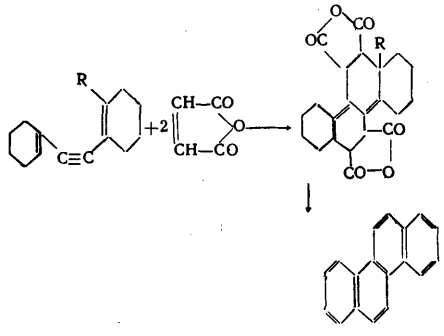
17. DIENE SYNTHESIS

Marvel and coworkers[48] were the first to establish that diisopropenylacetylene is capable of undergoing diene synthesis with maleic anhydride when a mixture of the two compounds in xylene solution is heated in the presence of aqueous alkali. However, these workers isolated an amorphous compound whose structure was not determined. Later, this reaction was studied in greater detail by other investigators[177], who showed that bicyclic compounds with methyl substituents (LIV) are indeed formed:



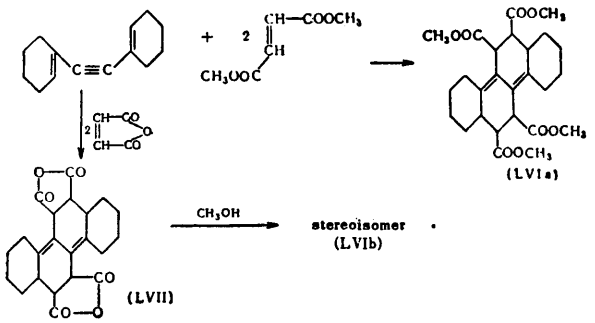
(LIV)

Subsequently this method was used for the synthesis of compounds of the hydrochrysene series with angular methyl groups. It was shown that condensation of di-Δ^1-cyclohexylacetylene (or its 2-methyl derivative) with two molecules of maleic anhydride yields the tetracyclic adduct (LV), whose decarboxylation and dehydrogenation give chrysene[178]:

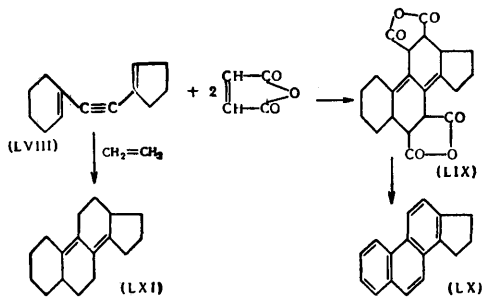


(LV)

where R = H, CH_3. Dicyclohexylideneacetylene undergoes diene synthesis with maleic anhydride[179] and dimethyl fumarate[180]. The resulting ester (LVIa) proves to be the stereoisomer of the ester (LVIb), which was obtained by the reaction of methanol with the adduct (LVII):

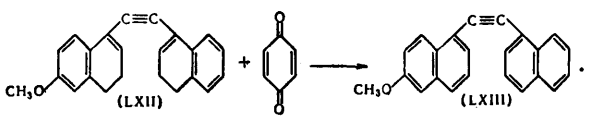


The addition of dienophiles to dienynes was studied in detail by Butz and coworkers[181,182]. Δ^1-Cyclohexenyl-Δ^1--cyclopentenylacetylene (LVIII) also undergoes diene synthesis with the formation of the adduct (LIX) whose structure was demonstrated by dehydrogenation, using palladium on carbon, to 15,16-dihydro-17*H*-cyclopenta[*a*]phenanthrene‡ (LX):[181,182]



Condensation of the dienyne (LVIII) with ethylene yields the tetracyclic compounds (LXI).

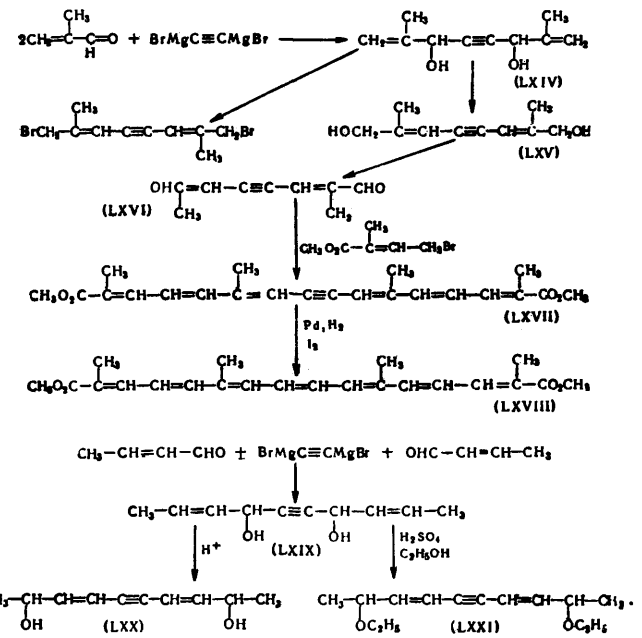
It is interesting to note that, when an attempt is made to condense the dienyne (LXII) with *p*-benzoquinone[183], instead of the expected reaction dehydrogenation of the dienyne with the formation of the aromatic compound (LXIII) occurs:



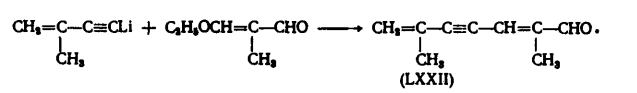
18. ALDEHYDES AND GLYCOLS OF THE DIVINYLACETYLENE SERIES

Aldehydes of the divinylacetylene series have been prepared for the synthesis of carotenoid compounds[184-187]. The synthesis was achieved as follows. Reaction of α-methylacrolein with acetylene di(magnesium bromide) gave the corresponding diol (LXIV) which was subjected to anionotropic isomerisation to give the divinylacetylene glycol (LXV) in good yield. Oxidation of the latter with manganese dioxide gave the divinylacetylene aldehyde (LXVI), whose condensation with methyl α-methyl-β-bromoethylacrylate followed by selective hydrogenation of the resulting dehydrocrocetin (LXVII) gave a good yield of the dimethyl ester of 8,8-*cis*--crocetin (LXVIII).

By reaction of crotonaldehyde with the acetylene di(magnesium bromide) derivative, Heilbron and coworkers[186] obtained the corresponding acetylene glycol (LXIX). The latter was subjected to anionotropic isomerisation to yield deca-3,7-dien-5-yne-2,9-diol (LXX). When this isomerisation was carried out in an alcoholic solution of sulphuric acid, 2,9-diethoxydeca-3,7-dien-5-yne (LXXI) was obtained:



Quite recently Yanovskaya and Kucherov[187] obtained 2,6-dimethylhepta-2,6-dien-4-yn-1-al (LXXII) in 20% yield by condensation of β-ethoxy-α-methylacrolein with isopropenylethynyllithium in ethereal solution followed by hydrolysis of the product with acetic acid in the presence of sodium acetate:



‡ See formula (XXIX) on p.249 (Ed. of Translation).

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THE MULTIPLET THEORY OF CATALYSIS — ENERGY FACTORS IN CATALYSIS

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An earlier review[1] has surveyed work on the principle of structural correspondence in the multiplet theory of catalysis. However, this principle alone is insufficient according to the theory. Thus ThO_2 and CaF_2 have the same structure, but different catalytic effects on alcohols[2]. A second principle which follows from the multiplet theory — that of energetic correspondence — will be examined below.

1. FUNDAMENTAL EQUATIONS OF THE MULTIPLET THEORY

Spatial (structural) and energetic factors in catalysis are linked by potential-energy curves. Fig. 1 shows such a curve for the chemisorption of an atom A on the surface of a catalyst K. The x axis is taken to pass through the centre of the sorbed atom A and be normal to the plane of the catalyst surface KK. On the atomic scale the profile of the surface is represented by the wavy line ZZ. The adsorbed atom A will be in a more stable position in the trough K' between the surface atoms[1]. In Fig. 1, therefore,

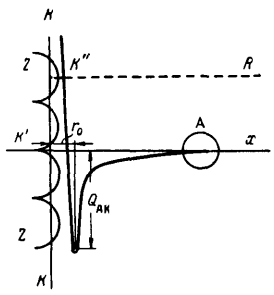


Fig. 1. Diagrammatic potential-energy curve for the chemisorption interaction of an atom A with the surface of a catalyst. This curve is to be imagined as lying in a plane perpendicular to the plane of the paper.

the horizontal axis must be drawn through the point K'. If this axis is displaced to the parallel position $K''R$, the form of the corresponding potential-energy curves will, of course, be different. However, it is the configuration in Fig. 1 which will have the decisive role, and to this approximation we shall regard Q_{AK} as the energy of bonding with the surface, and r_0 as the bond length (see Fig. 1).

Infrared spectra show[3] that hydrogen chemisorbed on platinum includes both weakly and strongly adsorbed atoms (H_w and H_s respectively). Pliskin and Eischens represent this by the scheme

$$\begin{matrix} H_w & & H_w \\ | & & | \\ Pt & H_s & Pt \end{matrix} \qquad (1.1)$$

which is consistent with Fig. 1, H_w being adsorbed at the sites K'', and H_s at K'.

Let us compare the energy of the bond A–B in the AB *molecule* when the latter is present in the gas and when it is chemically adsorbed on a catalyst surface as the atoms A and B. Let us denote by Q_{AB} the energy of the A–B bond in the gas, and by Q_{AK} (see above) the energy of the A–K bond between the A atom and the catalyst. (Henceforward Q_{XY} will always denote the energy of the X–Y bond.)

According to the multiplet theory, the energy $E_{AB,K}$ required to cleave the bond A–B into atoms adsorbed on the catalyst will differ from Q_{AB}. By definition we have the thermochemical equation

$$A{-}B + 2K = A[K] + B[K] - Q_{AB,K} \qquad (1.2)$$

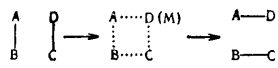
where A[K] and B[K] represent A and B atoms adsorbed on the catalyst K. We also have the self-evident thermochemical equations A–B = A + B – Q_{AB}; A + K = A[K] + Q_{AK}; B + K = B[K] + Q_{BK}, summation of which gives

$$A{-}B + 2K = A[K] + B[K] - Q_{AB} + Q_{AK} + Q_{BK}. \qquad (1.3)$$

From Eqns. (1.2) and (1.3) we find that

$$E_{AB,K} = -Q_{AB} + Q_{AK} + Q_{BK}. \qquad (1.4)$$

Thus the A–B bond will be weakened on the catalyst compared with the gas. The quantity $E_{AB,K}$ is the heat of chemisorption of the molecule A–B on the catalyst. If $Q_{AB} > Q_{AK} + Q_{BK}$, this will be a case of a negative heat of adsorption, recently considered by de Boer[5]. Two bonds are involved in the duplet reaction[1]



(1.5)

Surface atoms of the catalyst and substituents attached to A, B, etc. are omitted from this scheme, the physical meaning of which is discussed in Ref. 1.

As above, the heat of formation of the multiplet complex M will be

$$E' = -Q_{AB} - Q_{CD} + (Q_{AK} + Q_{BK} + Q_{CK} + Q_{DK}), \qquad (1.6)$$

and the heat of decomposition of M into the reaction products[6,7]

$$E'' = Q_{AD} + Q_{BC} - (Q_{AK} + Q_{BK} + Q_{CK} + Q_{DK}). \qquad (1.7)$$

The quantity $-E'$ is the height of the energy barrier to the reaction, and the same applies to $-E''$. If $-E'$ is lower than $-E''$, the multiplet complex will break down more often into the starting materials than into the reaction products, and the reaction will go with difficulty or not at all. If, however, the barrier $-E''$ is lower than $-E'$, the multiplet complex will break down into the reaction products, which will evaporate from the surface. The catalyst atoms are thereby disengaged, and again become ready to exert their catalytic effect. The cause of catalysis here is the lowering of the energy barrier resulting from the weakening of bonds on the catalyst compared with the gas phase — see Eqns. (1.6) and (1.7).

The overall reaction velocity is limited by the height of the energy barrier $-E$, where E represents E' or E'', whichever is the more negative:

$$E = \min(E, E'', L). \qquad (1.8)$$

In general $L = 0$, but as a result of complicating factors L may have a constant (small) value differing from zero — *cf.* Eqn. (1.9). The greater is E, the lower is the energy barrier, and the higher the reaction velocity (below the Schwab inversion point).

Soon after the appearance of a paper on the multiplet theory[7], Polanyi published[8] a very similar theory of catalysis, which provided a quantum-mechanical basis for views analogous to those underlying Eqns. (1.6) and (1.7) of the multiplet theory. Polanyi agrees with London[9] that a gaseous reaction AB + CD = AD + BC is hindered by the existence of the repulsion inherent in the nature of chemical valency forces: thus the atom A combined with B repels any other atom, for example D. For reaction to occur, the molecules AB and CD must come together with A beside D, and B beside C. In such a position, however, calculation shows the repulsive forces to be a maximum. On the other hand, the activation energy of a reaction involving a molecule and a free atom is small. According to Polanyi, free valencies project from the catalyst surface, and act as free atoms, which greatly facilitates double decomposition between AB and CD. This part of Polanyi's paper[8] can be regarded as a quantum-mechanical demonstration of the fundamental assumptions of the multiplet theory. Furthermore, Polanyi's arguments show why in endothermic reactions the energy barrier is little higher than the negative heat of reaction: this follows from the similarity to free-radical reactions.

In contrast to Ref. 7, however, Polanyi's paper[8] gave no formulae and no applications to actual reactions. He

did this only in 1935,[10] when he examined one reaction, the para–ortho conversion of the hydrogen molecule. The formulae given for this case were the same as Eqns. (1.6) and (1.7). Temkin[11] developed Polanyi's theory, and in 1957 obtained[11] the same equations (1.6) and (1.7) as the Reviewer, obviously because of the similarity of the main premises.

However, in addition to the closeness of the views expressed in Refs. 8, 10, and 11 with those of the multiplet theory, there are also important differences, these papers assuming complete cleavage of the A–B and C–D bonds into radicals. In contrast to this, the multiplet theory assumed right from the start — as a development of the views of Mendeleev, Zelinskii, and Bodenstein on molecular deformation as a cause of catalysis[1] — that formation of the intermediate complex does not necessarily involve complete rupture of chemical bonds[6,7]. It was specially stressed[12] that the complete "dissociation" assumed in Eqns. (1.6) and (1.7) "measures the deformation of the molecules".

The quantitative relation between the heat of formation (or decomposition) E of the multiplet intermediate complex and the activation energy ϵ is given by the formula

$$\varepsilon = A - \gamma E. \qquad (1.9)$$

In 1946 the Reviewer[13] suggested Eqn. (1.9) with values of $\gamma = \frac{3}{4}$ and $A = 0$, and applied it to endothermic reactions of dehydrogenation and dehydration. In 1955 Semenov[14] examined a large quantity of experimental data on the reaction AB + C = AC + B, involving free atoms and radicals, and found Eqn. (1.9) to be applicable. It is interesting that Semenov finds the same value of $\gamma = \frac{3}{4}$ for endothermic reactions as does the Reviewer; for exothermic reactions $\gamma = \frac{1}{4}$. The constant A is small (11.5 kcal). With different materials and a different notation, Eqn. (1.9) is known as the Brønsted equation.

Eqn. (1.9) can be interpreted qualitatively on the basis of the theory of rate processes[15]. The electron pairs in the molecules AB and CD are delocalised in the resulting activated complex M, and are then localised afresh in the reaction products. When the reaction velocity is controlled by the adsorption stage, the activation energy ϵ is lower than E, the energy of complete rupture of the bonds A–B and C–D, because of the energy gained from the incipient formation of the bonds A–D and B–C; the stronger are these new bonds, the lower will ϵ be. The chemical reaction takes place at this point, when equilibrium is disturbed. If, on the other hand, the reaction velocity is controlled by the desorption stage, an increase in the energy of the bonds A–D and B–C results in an increase in ϵ.

What has been stated previously[1] about the similarity between the multiplet theory and the theory of rate processes[15] as applied to catalysis can be supplemented by the following common features of the two theories. (1) In a reaction the new bonds begin to be formed before the old bonds on the surface have been complete broken: *i.e.* molecules do not usually break down into radicals. In this respect the theory of rate processes diverges from the standpoint of Polanyi's previous theory[8,9]; such a view was adopted in the multiplet theory from the start (see above). (2) Potential-energy curves are considered, in detail in the theory of rate processes (potential-energy surfaces), and in the multiplet theory points on these curves corresponding to the bond lengths and energies are taken. (3) The theory of rate processes demonstrates that chemisorption, for example of a hydrogen molecule on carbon[16] or on nickel[17], occurs at the two atoms, as is assumed in the multiplet theory. (4) In several cases the structures of active and multiplet complexes are identical, for example in the dehydrogenation of alcohols[18], and then the theory of rate processes enables the reaction velocity to be calculated from the model given by the multiplet theory (see preface to Ref. 15). Both theories are based on theories of the structure of matter, but the theory of rate processes, which has the wider scope, proceeds by deduction from quantum mechanics, whereas the multiplet theory is obtained inductively by generalising experimental results on catalysis, taking into account the theory of the structure of matter.

Eqns. (1.6)–(1.9) form the main energy equations of the multiplet theory. They enable the comparative ease of occurrence of a reaction to be assessed if the bond energies Q are known. The latter depend on the nature of the bonds and the catalysts. In fact, ϵ can be calculated from Q by means of Eqns. (1.6)–(1.9). After substitution for ϵ in the Arrhenius equation, bearing in mind the compensation effect, we obtain

$$k = \kappa e^{\varepsilon\left(h - \frac{1}{RT}\right)} \qquad (1.10)$$

whence we find the rate constant k since the parameters κ and h remain fairly constant for reactions and catalysts of the same type[19]. The approximate character of such calculations must be realised, but nevertheless they are broadly correct.

If we now regard Q_{AK}, Q_{BK}, ... as variables, we can transform Eqns. (1.6)–(1.9) into a form convenient for the consideration of problems of catalyst selection, the central problem of catalysis. Let us examine the duplet reaction (1.5) and write its heat of reaction as $u = -Q_{AB} - Q_{CD} + Q_{AD} + Q_{BC}$, the total energy of the bonds broken and formed as $s = Q_{AB} + Q_{CD} + Q_{AD} + Q_{BC}$, and the adsorption potential energy as $q = Q_{AK} + Q_{BK} + Q_{CK} + Q_{DK}$. Then Eqns. (1.6) and (1.7) become

$$E' = q - \frac{s}{2} + \frac{u}{2} \qquad (1.11)$$

for adsorption, and

$$E'' = -q + \frac{s}{2} + \frac{u}{2} \qquad (1.12)$$

for desorption. Eqns. (1.11) and (1.12) are illustrated graphically in Fig. 2 for endothermic (I) and exothermic (II) reactions. The coordinates of the maximum are

$$E_0 = u/2, \quad q_0 = s/2. \qquad (1.13)$$

The straight lines have a slope of 45°, since the coefficients of q are unity. On the basis of Eqn. (1.8) the lower portions of these straight lines are chosen (the thick lines). They form what have been termed "volcano-shaped curves", and can be expressed also in analytic form[13] by the use of Dirichlet's discontinuity factor. In Fig. 2 FH is the height

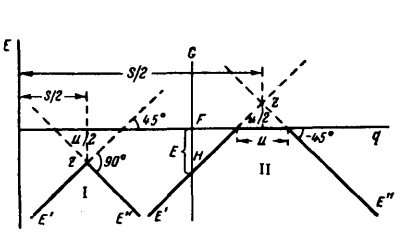


Fig. 2. Volcano-shaped curves (for key see text).

of the energy barrier $-E$, which is lowest at the maximum, *i.e.* when $E' = E''$.

The condition for selection of the optimum catalyst (in case I) is evidently that the adsorption potential energy q should be the mean $s/2$ of the values for the broken and new bonds. The optimum height of the energy barrier is then half the heat of reaction $u/2$ for the catalytic reaction. Thus it follows from the multiplet theory that energetic as well as structural correspondence must exist in catalysis. The principle of energetic correspondence is expressed mathematically by the equation

$$q = s/2. \qquad (1.14)$$

which has been subsequently obtained also by Temkin[11].

This method enables us to reach the practically significant conclusion whether a given catalyst is the most active possible for a given reaction, or whether it can be further improved. For this purpose the activation energy ϵ must be determined experimentally, and from it E found. If E differs greatly in magnitude from $u/2$, the catalyst can still be improved on. However, the condition $E = u/2$ does not signify the limit of activity, since it is still possible to change the reaction mechanism.

The catalyst should be not only the most active but also the most selective. Let us therefore examine the condition for the preferential occurrence of one reaction in the model case of the two reactions (I) and (II). Instead of the one volcano-shaped curve of Fig. 2, we shall now have two such curves and two intersecting lines (Fig. 3). In order to make the discussion more concrete, let reaction (I) be dehydrogenation and (II) dehydration of an alcohol on nickel. Here all quantities are known (including E from Table 4, below), and Fig. 3 can be drawn to scale. Since the point of intersection H lies considerably above H', dehydrogenation is decisively predominant, in agreement with experiment. The limit of sensitivity of the analytical method employed is provided by the lower boundary AB of the reaction zone $ABqO$.

The activity (and sensitivity) of a catalyst having a given $q = q_1$ can be raised by varying the components Q_{AK}, Q_{BK}, Q_{CK}, and Q_{DK} (the intercepts on the horizontal axis in Fig. 2) in such a way that q_1 approaches closer to the optimum condition $q = s/2$. If, therefore, $q_1 < s/2$, the reaction velocity will increase when

$$0 < \Delta q_1 < s - 2q_1. \qquad (1.15)$$

The first method for achieving this is to replace one of the atoms in the multiplet by another. The employment of mixed catalysts is relevant here, reaction often taking place at the interface between two phases. Condition (1.15) is a quantitative formulation of the enhanced activity of boundaries. Another method for increasing the activity and selectivity of catalysts is to change the nature, number, and arrangement of atoms in the catalyst adjacent to the active centre (see Section 6).

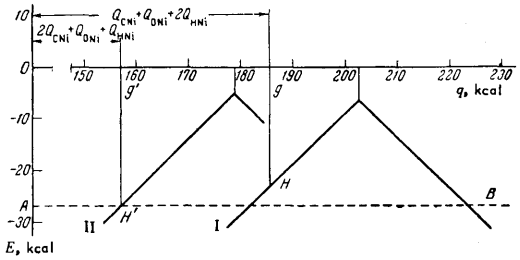


Fig. 3. Volcano-shaped curves for alcohols (drawn to scale): I) dehydrogenation; II) dehydration.

2. BOND ENERGIES

In order to apply the equations of the multiplet theory, it is necessary to know energies of bonding with the catalyst Q_{AK}. These can be found experimentally by thermochemical, comparative, and kinetic methods. Adsorption methods[20,21] and calculation[22] have also been proposed, but are as yet little developed, and have not found practical application.

Thermochemical Method

In this method Q_{AK} is found from the bulk heats of formation U of compounds. We shall regard such replacement of surface by bulk properties as legitimate if the sublimation term is taken into account (see Section 6). The term "thermochemical" is to be understood in a broader sense: U can be obtained not only calorimetrically but also, for example, by a spectroscopic method. However, the calculations involve an additive procedure based on Hess's thermochemical law.

Comparative Method

In this method[4,6,7,23] comparison is made of the relative rates of reactions of the same type involving different bonds in the same molecule on a given catalyst. Application of Eqns. (1.6) and (1.7) of the multiplet theory to a set of such molecules and bonds enables a series of inequalities to be set up, from which the relative magnitudes of Q_{AK} can be established to within 1 kcal. The zero on the scale is obtained by comparing one of the bond energies thus obtained for this system, for example Q_{HNi}, with the value found by the thermochemical method.

System of Q Values Adopted

Combination of the above two methods yields a set of bond energies (Table 1) which are important for organic catalysis. In Table 1 values of Q obtained earlier[6,4,23] have been recalculated on the basis of the new energies of atomisation of carbon and nitrogen. Cottrell's data[24] (1958)

TABLE 1. Energies of atomisation A (at 25°) and bond energies Q_{AB} and Q_{AK}, kcal.

A	C	N	O	H	Cl	Br	
	170.9	112.9	59.5	52.1	28.9	26.7	
Q	C	N	O	H	Cl	Br	C = π bond
C	82.6						63.2
N	72.8	75.3*					74.2
O	85.5	53	35				92.0
H	98.7	93.4	110.6	104.2			
Cl	81	46	52	103.1	57.9		
Br	68	—	48	87.4	—	46.1	
Ni	14	27	48.5	55	67	54	=C—Ni 27

* From Ref. 25.

are taken as more recent and more detailed for energies of atomisation A, *i.e.* the heats of formation of the gaseous atoms from the elements in their standard state (see upper part of Table 1), and for the thermochemical bond energies in the molecules Q_{AB}. They are almost identical (except for a few) with Kondrat'ev's data[25] (1957) and with the calculated values in Ref. 26.

The last column of Table 1 contains the energies of breaking the first reactive bond C=C, C=N, and C=O. The new information supplied by the Reviewer[6,23] relates to the energy of bonding the reactant atoms to the most thoroughly studied catalyst, nickel (Q_{ANi} — see bottom line in Table 1 — for the solid state, starting from solid nickel). The Q_{ANi} values for the bonds formed by nickel with chlorine and bromine were calculated from recent thermochemical data on the heats of formation of $NiCl_2$ and $NiBr_2$ and from the energies of atomisation in Table 1. The energy of the Ni–H bond was determined also from NiH_2 and NiH[27] and found to be 55 kcal. The energies Q_{ANi} for the bonds of Ni with C, N, and O were obtained by the above comparative method. With fixed values of Q_{HNi}, Q_{ClNi}, and Q_{BrNi} such comparison fixes the values of Q_{CNi}, Q_{NNi}, and Q_{ONi} to within 1 kcal. The value thus obtained for Q_{ONi} = 48.5 is below the thermochemical value of 59 kcal (from NiO), probably because of the sublimation term (see Section 6). No thermochemical data are yet available for Q_{CNi} and Q_{NNi}, but the values obtained (Table 1) arrange themselves in the sequence C < N < O, in agreement with the data of inorganic chemistry.

As in any additive scheme (in the case of molecular refraction, for example) constitutional corrections must be made. The value of Q_{CNi} = 14 kcal is applicable to reactions in which no double bond is either formed or broken, for example in the hydrogenolysis of ethane. The value of Q_{CNi} = 27 kcal applies to a carbon atom linked by a double bond with a neighbouring C, N, or O atom in the molecule either inside or outside the indicial group: this is the value to be used in the hydrogenation of a double bond, as well as for dehydrogenation, since the reverse reaction passes through the same intermediate state as does the forward reaction. With further refinement it may perhaps be necessary to introduce similar corrections for a double bond with the atoms N, O, and S.

The bond energies Q are fairly strongly affected by substituents. Thus the values of Q for the C=O double bond in HCHO, RCHO, and R_2CO are 166, 176, and 179 kcal respectively. The data in Refs. 23 and 24 show that a strong substituent effect is the rule, not an exception. However, this fact is of no great importance in catalysis, since substituents have similar effects on Q_{AB} and Q_{AK}, and these quantities occur in both Eqn. (1.6) and Eqn. (1.7), with opposite signs. In catalysis, therefore, the effects of substituents often cancel out (*cf.* Section 4).

From time to time, with improvements in experimental accuracy, the values of A, the dissociation energies D of the elements (for example N_2), and the sublimation energies (of solid carbon) have been revised, and therefore the system adopted for Q has changed (see Refs. 6, 4, and 23 as well as the present review). Nevertheless, this should not affect E. In fact

$$Q_{AB} = D_{A_2}/m + U_{AB} + D_{B_2}/n, \quad (2.1)$$

$$Q_{AK} = D_{A_2}/m + U_{AK}, \quad (2.2)$$

$$Q_{BK} = D_{B_2}/n + U_{BK}, \quad (2.3)$$

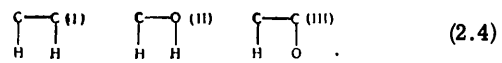
where the U (also additive) are the energies of bond formation, not from the atoms (like the Q) but from the molecules or the solids, while m and n are valencies. When Eqns. (2.1)–(2.3) are substituted in Eqn. (1.4), the D cancel out, as does also the sublimation energy. The thermochemical quantities U, however, remain unchanged. The data given below correspond to the Q values in Table 1.

The heats of reaction should be based on the absolute zero, since elementary processes are being considered. However, the fact that they have actually been found for 298°K does not entail substantial corrections, since multiplet complexes on a surface form a condensed system.

Kinetic Method

First variant. The method consists[13] in determining on a given catalyst the activation energies ϵ of as many reactions as there are different kinds of atoms in the given duplet indicial groups. This gives as many equations (1.6) as there are unknown Q_{AK}.

The first variant is more suitable for oxide catalysts. Here we have a square matrix of the coefficients in a set of linear equations. The dehydrogenation of hydrocarbons (I), dehydrogenation of alcohols (II), and dehydration of alcohols (III) provide a convenient group of reactions. On oxides the reactions (II) and (III) usually occur simultaneously. Here the indicial groups are



(2.4)

Fig. 4 (from Ref. 41) illustrates volcano-shaped curves (to scale) for these reactions. The vertical distances between such a curve and the horizontal axis represent the E values. Such vertical lines are drawn on the left, not on the right, of the maxima, as in the case of nickel (Fig. 3), where theoretical calculation has shown that $E = E'$, not E'', for $E' > E''$ (Table 4). From the set of equations of the type of Eqn. (1.6) for the reactions (I)–(III) together with the equation

$$\varepsilon = -0.75\,E' \quad (2.5)$$

based on Eqn. (1.9), we find that

$$Q_{HK} = \tfrac{1}{3}(-\varepsilon_1 - 2\varepsilon_2 + 2\varepsilon_3) + \tfrac{1}{2}(Q_{CH} - Q_{CO} + Q_{OH}), \quad (2.6)$$

$$Q_{CK} = \tfrac{1}{3}(-\varepsilon_1 + 2\varepsilon_2 - 2\varepsilon_3) + \tfrac{1}{2}(Q_{CH} + Q_{CO} - Q_{OH}), \quad (2.7)$$

$$Q_{OK} = \tfrac{1}{3}(3\varepsilon_1 - 2\varepsilon_2 - 2\varepsilon_3) + \tfrac{1}{2}(Q_{CH} - Q_{CO} - Q_{OH}). \quad (2.8)$$

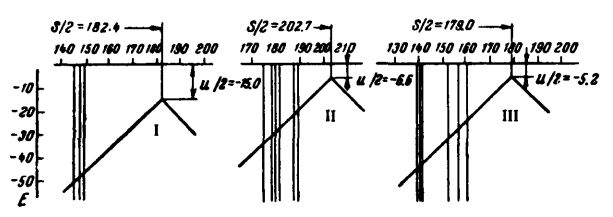


Fig. 4. Vertical intercepts from horizontal axis to volcano-shaped curves representing heights of energy barriers – E found experimentally (drawn to scale) for:
I) dehydrogenation of hydrocarbons; II) dehydrogenation of alcohols; III) dehydration of alcohols.

Substituting known values of Q_{CH}, Q_{CO}, and Q_{OH} from Table 1 (identical with those in Ref. 24), we obtain values of 62.0, 36.8, and 48.6 respectively for the second groups of terms (containing the Q) on the right-hand sides of Eqns. (2.6)–(2.8). By means of these equations we can find from the activation energies the energies of bonds between hydrogen, carbon, or oxygen atoms and the catalyst.

Examples of the results[28-56] are given in Table 2 in the form of the values of Q_{AK} found for catalysts prepared by the same method (precipitation by ammonia from nitrate solution) when tetralin and isopropanol (usually) are passed over them†. The method used for the kinetic determinations has been described previously[47]. Experiments have shown that the activation energy ϵ is practically the same for identical indicial groups with different substituents on the same catalyst. This confirms that the molecules are oriented in the reactions with these particular indicial groups towards the catalyst, in conformity with the multiplet theory. The values obtained for the energy of bonding with the catalyst are of reasonable magnitude. No incongruities, in the shape of negative, too large, or, on the other hand, nearly zero values, are found.

It is very significant that, on the average, energies of bonding with different oxides (Table 2) are comparable with the corresponding values for nickel obtained by the combined–comparative and thermochemical methods (*cf.* Table 2 with the bottom row in Table 1).

The values obtained for Q_{OK} show that in oxides the active centre consists (at least predominantly) of metal atoms, not oxygen. Indeed, firstly we would otherwise have a peroxy--bond, which is, however, weaker (Q_{O-O} = 35 kcal); and secondly Q_{AK} has similar values for MoO_{3-x} and MoS_2 (Q_{HK} = 61.0 and 60.3; Q_{CK} = 27.7 and 26.8; Q_{OK} = 42.9 and 52.5 kcal respectively).

Similar methods are used to find the energy of bonding of nitrogen with the catalyst ThO_2 (Q_{NThO_2} = 31.8 kcal). Thus $Q_{CK} < Q_{NK} < Q_{OK}$, in agreement with other chemical results.

Adsorption potentials q can also be determined. For cyclohexane and Cr_2O_3 we thus have q = 167.2 kcal, which is still quite far from the maximum on the volcano-shaped curve, for which q_0 = 182.4 kcal from Eqn. (1.13). Hence theory indicates that the catalyst can still be improved. Table 2 will be discussed in greater detail in Section 5.

TABLE 2. Bond energies Q_{AK} with oxide catalysts, kcal.

Atomic No.	Oxide	Q_{HK}	Q_{CK}	Q_{OK}	Ref.	Atomic No.	Oxide	Q_{HK}	Q_{CK}	Q_{OK}	Ref.
4	BeO	49.8	19.6	66.8	32	42	MoO_{3-x}	61.3	27.7	42.9	42
22	TiO_2	60.5	28.6	46.3	38	57	La_2O_3	47.5	17.2	64.9	36
23	V_2O_3	56.4	26.7	42.5	46	58	CeO_2	57.6	19.8	49.9	36
24	Cr_2O_3	60.9	22.7	51.8	33	59	Pr_2O_3	52.9	11.4	72.0	36
25	MnO	50.7	26.7	38.8	34	60	Nd_2O_3	52.8	16.0	64.7	36
30	ZnO*	48.6	23.1	61.7	45	64	Gd_2O_3	54.8	15.0	65.2	36
31	Ga_2O_3	62.8	24.9	50.6	44	74	WO_{3-x}	52.6	27.6	43.5	35
39	Y_2O_3	53.6	22.1	58.8	39	90	ThO_2	52.3	21.6	61.3	40
40	ZrO_2	61.3	11.8	29.8	29	92	U_3O_8	48.9	25.6	40.3	41

* Obtained by the second variant of the kinetic method.

† Where previous values of Q_{AK} were based on Q_{AB} values from Ref. 23, conversion to the new Q_{AB} system (Table 1) is effected by adding 8.3 kcal to Q_{CK}. No changes are required in Q_{HK} and Q_{OK}.

If the law of mass action is regarded as the first stage of generalisation in catalytic kinetics, the adsorption isotherm as the second stage, application of the Arrhenius and Frenkel' equations to the temperature dependence of the rate constants and adsorption coefficients respectively as the third stage, and consideration of surface heterogeneity and in particular the compensation effect as the fourth stage, the resolution of the activation energy into its component bonding energies in accordance with Eqns. (1.6) and (1.9) can rightly be regarded as a higher, fifth stage of generalisation in the kinetics of reactions subject to heterogeneous catalysis.

Second variant. The second variant of the kinetic method which has been developed[48-52] is also based on the application of Eqns. (1.6) and (2.5) of the multiplet theory, and is most applicable to metallic catalysts. Here the matrix of the coefficients is no longer square but triangular. The first step is to determine Q_{HK} for the para–ortho conversion of H_2, whose indicial group contains atoms of only one kind

(2.9)

Therefore one reaction is sufficient to determine the energy of bonding of hydrogen with a catalyst if the activation energies ϵ have been found experimentally. The latter can be taken from published data. In Eqn. (1.6) let us substitute H for A, B, C, and D, and Ni for K. Then from the known ϵ_1 = 5.9 and Q_{H-H} = 104.2 kcal, together with Eqn. (2.5), we find that

$$Q_{H-Ni} = \frac{1}{2}Q_{H-H} - \frac{1}{3}\epsilon_1 \simeq 50.1 \text{ kcal}. \qquad (2.10)$$

(Similarly, from the ortho–para conversion of deuterium, where Q_{D-D} = 106.0 kcal, we obtain Q_{D-Ni} = 50.1 kcal.)

The next step is calculation for a reaction whose duplet indicial group contains hydrogen together with another type of atom, and for which Q_{HNi} has already been found. Such a reaction may be the hydrogenation of ethylene, having the index

(2.11)

Proceeding as before, we find that

$$Q_{=CNi} = \frac{1}{2}(Q_{C=C} + Q_{H-H}) - Q_{H-Ni} - \frac{2}{3}\epsilon_3, \qquad (2.12)$$

where ϵ_3 = 8.2 and $Q_{C=C}$ = 63.2 kcal (energy of rupture of the π bond). On substituting the known values of Q_{HK} and Q_{HNi}, we obtain Q_{CNi} = 28.1 kcal; from other data we obtain a value of 26.8 kcal. The isotopic exchange of ethylene with deuterium yields the not greatly differing value of 31.5 kcal.

By continuing in this way with reactions in whose indicial group new atoms are continually appearing, it is possible to find the energies of bonding of nickel with the various elements in organic compounds. Apart from the above reactions, such calculations have been made for the hydrogenation of propene, acetylene, and propyne, the hydrogenolysis of ethane and methylcyclopropane, and deuterium exchange with methane, water, isopropanol, ammonia, etc. The results[52] are listed in Table 3.

TABLE 3. Bond energies Q_{AK} with metallic catalysts, kcal.[52]

	H	D	−C	=C	≡C	ΔC	O	N
Ni	50.1	50.1	16.0	28.1	42.7	31.8	57.7	29.3
Fe	49.4	50.2	15.0	27.5	—	30.1	58.9	32.1
Pt	54.2	55.2	13.5	22.3	36.6	28.8	34.3	27.4
Pd	53.3	54.3	13.8	23.5	38.0	31.3	44.1	25.1

The bond energies found by this form of the kinetic method are remarkably close to those obtained by a quite different method (Table 1) long before the activation energies had been determined. Thus the values obtained by the two methods for the bonding energy (in kcal) of nickel are respectively — 50.1 and 55 with H, 16.0 and 14 with C, 28.1 and 27 with C, 57.5 and 48.5 with O, and 29.3 and 27 with N (*cf.* Tables 3 and 1). The fact that two independent methods yield the same results provides convincing evidence of the correctness of the theory.

In almost all cases with nickel the adsorption potential energies q calculated from the activation energies are close to the maximum values of $s/2$. Hence the activity of nickel catalysts is close to the maximum.

Values of Q_{AK} for platinum, palladium, and iron calculated in a similar manner are included in Table 3.

3. EFFECT OF EXTRAINDICIAL ATOMS

Hydrogenolysis on Nickel

The Q_{AK} values in Table 1 can be used to give a quantitative prediction of the reaction products. Let us first consider hydrogenolysis[6,4,22,53], which is specified by the index

(3.1)

Here variation occurs only in the left-hand portion, the atoms A and B. We shall regard a reaction as taking place more readily than another if it occurs at a lower temperature. Table 4 gives (above) the indices (3.1) of reactions over nickel arranged in the observed sequence of increasing ease of occurrence. The sequence based on Q_{AB} (see first row of numerals in Table 4) is evidently quite different, the numbers fluctuating without any regularity.

In contrast, the required sequence in ease of reaction on nickel is strictly observed by the values of E calculated from Eqn. (1.6). In Table 4 all the E values for hydrogenolysis do in fact increase from left to right, in agreement with experiment.

TABLE 4. E_{calc} for reactions on nickel catalyst, kcal.

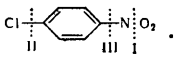
C H | | C H	C H | | N H	C H | | O H	N H | | N H	C H | | Cl H	C H | | Br H	O H | | O H	N H | | O H
$Q_{AB}=82.6$	72.8	85.5	75.3	81	68	35	53
$E'=-48.8$	−26.0	−17.2	−15.5	5.8	5.8	$E''=14$	$E''=18.5$
C—C | | H H	N C | | H N	C—N | | H H	C—C | | H O	C C | | H C	C—C | ‖ H C	C—O | | H H	C H ‖ | N H
$E'=-33.4$	−30.2	−28.1	−26.4	−25.9	−25.9	−23.8	−14.4

Calculation of E from Eqn. (1.6) shows also that multiple bonds A=B and A≡B should first be hydrogenated to a single bond A–B, after which the hydrogenolyses listed in Table 4 can begin. Therefore Table 4 is suitable also for compounds containing multiple bonds.

Let us now consider the hydrogenolysis of a multifunctional molecule, *i.e.* one containing different C–N, C–O, C–Cl, etc. bonds. Such a molecule can react in different ways. The question can be posed as to which type of bond will be the first to be broken, which the second, etc. The less stable a bond, the lower the temperature at which it is ruptured. Hydrogen adds on to the valencies which are set free on rupture. What substances can be formed on cleavage? And on what properties of the given molecules and catalyst does this sequence depend?

Experiment shows that Table 4, in particular the top row, gives unambiguously the sequence of ease of hydrogenolysis. This is important evidence in support of the multiplet theory. Since the molecule is oriented with the ruptured bonds towards the catalyst, Table 4 conveys also the orientation of the molecules at different temperatures.

As an example we can consider more fully the hydrogenolysis of *p*-chloronitrobenzene over nickel[54]



According to theory, the N–O bond (E = 18.5 kcal mole^{-1}) should be the first to be broken, then the C–Cl bond because it has a lower E (5.8), after this the C–N bond (-26.0), and only then the C–C bond (-48.8). Analysis of the reaction products at increasing temperatures showed that the predictions of theory are completely confirmed by experiment: *p*-chloroaniline and water are first obtained, then aniline and HCl, then benzene and NH_3, and finally CH_4.

The multiplet theory bases the sequence of hydrogenolysis in Table 4 on a vast number of experimental data, as is evident from Table 5, which gives results of calculations

TABLE 5. Sequence of hydrogenolysis reactions on nickel.

Class of compounds	Compound	Products: A) expected; B) observed
Amides	$CH_3\cdot CO\cdot NH_2$	A. 1) $CH_3CH_2NH_2$; H_2O; 2) CH_3CH_3; NH_3; 3) CH_4 B. 1) $CH_3CH_2NH_2$; H_2O; 2) CH_3CH_3; NH_3; 3) CH_4
Nitroalkanes	$CH_3\cdot CH_2\cdot NO_2$	A. 1) $CH_3CH_2NH_2$; H_2O; 2) CH_3CH_3; NH_3; 3) CH_4 B. 1) $CH_3CH_2NH_2$; H_2O; 2) CH_3CH_3; NH_3; 3) CH_4
Nitrites	$CH_3\cdot O\cdot NO$	A. 1,2) CH_3OH; NH_3; H_2O; 3) CH_4; H_2O B. 1,2) CH_3OH; NH_3; H_2O; 3) CH_4; H_2O
Ketoximes	$(CH_3)_2C{=}N\cdot OH$	A. 1) $(CH_3)_2C{=}NH \rightarrow (CH_3)_2CHNH_2$; H_2O; 2) $(CH_3)_2CH_2$; NH_3 B. 1) $(CH_3)_2C{=}NH \rightarrow (CH_3)_2CHNH_2$; H_2O; 2) $(CH_3)_2CH_2$; NH_3
Amines	$C_6H_4\cdot CH_2\cdot NH_2$	A. 1) $C_6H_5CH_3$; NH_3 B. 1) $C_6H_5CH_3$; NH_3
Aromatic alcohols	$C_6H_5\cdot CH_2\cdot OH$	A. 1) $C_6H_5CH_3$; H_2O B. 1) $C_6H_5CH_3$; H_2O
Aryl chlorides	$C_6H_5\cdot Cl$	A. 1) C_6H_6; HCl; 2) CH_4 B. 1) C_6H_6; HCl; 2) CH_4
Esters of chlorinated acids	$CH_2\cdot Cl\cdot COOR$	A. 1) CH_3COOR; HCl B. 1) CH_3COOR; HCl
Brominated arylamines	$BrC_6H_4\cdot NH_2$	A. 1) $C_6H_5NH_2$; HBr; 2) $C_6H_4\cdot NH_2$; 3) CH_4 B. 1) $C_6H_5NH_2$; HBr; 2) $C_6H_4\cdot NH_2$; 3) CH_4

analogous to the above example with chloronitrobenzene. Table 5 lists classes of compounds subjected to hydrogenolysis (taken from Sabatier's book[55]) and as examples one compound from each class, (A) indicating the products expected theoretically, and (B) the observed reaction products. The agreement with theory is seen to be excellent. The rule is obeyed by all the substances investigated with extremely rare exceptions. The following compounds‡ have been taken as starting materials — nitromethane, nitroethane, nitrobenzene, *o*- and *m*-nitrotoluenes, 1-nitronaphthalene, *m*-dinitrobenzene, 1,5-dinitrotoluene, nitrophenols, methyl nitrite, ethyl nitrite, propyl nitrite, isobutyl nitrite, isopentyl nitrite, acetaldehyde oxime, acetone oxime, ethyl methyl ketone oxime, methyl propyl ketone oxime, diisopropyl ketone oxime, diethyl ketone oxime, acetophenone oxime, ethyl phenyl ketone oxime, benzophenone oxime, phenyl propyl ketone oxime, cyclohexanone oxime, ethylcyclohexanone oxime, 3-methylcycloheptanone oxime, menthanone oxime, camphor oxime, acetamide, propionamide, ethyl isocyanate, ethylurea, phenyl isocyanate, aniline, toluidines, *N*-methylaniline, *N*-methyltoluidine, *NN*-dimethyltoluidine, *N*-ethylaniline, diphenylamine, benzylamine, ethylamine, pentylamine, hydrocyanic acid, acetonitrile, propionitrile, γ-methylvaleronitrile, methylmalononitrile, benzonitrile, *p*-tolunitrile, phenylhydrazine, azobenzene, benzyl alcohol, phenethyl alcohol, diphenylmethanol, phenyl-*p*-tolylmethanol, triphenylmethanol, 2-*p*-tolylpropan-2-ol, furfuryl alcohol, 2-methylfuran, benzaldehyde, methylcyclopentanone, dihydrocamphorone, succinic anhydride, phthalic anhydride, camphoric anhydride, phenol, cresols, xylenols, quinol, resorcinol, catechol, quinones, acetophenone, methyl *p*-tolyl ketone, *p*-butylphenyl methyl ketone, benzylacetone, benzophenone, benzyl phenyl ketone, dibenzyl ketone, 1,1-diphenylacetone, methyl 1(and 2)-naphthyl ketones, 1-naphthyl propyl ketone, hexahydroanthrone, benzil, benzoin, 1-phenylbutane-1,3--dione, anisole, methyl tolyl ethers, methyl 1-naphthyl ether, phenyl oxide, diethyl ether, cyclohexene oxide, cyclohexanone, methylcyclohexanone, cyclopentanone, acetone, chlorobenzene, dichlorobenzene, perchlorobenzene, chlorotoluene, trichlorophenol, chloroaniline, chloronitrobenzene, mono-, di-, and tri-acetic esters, bromobenzene, *p*-bromotoluene, bromoaniline, bromonitrobenzene, 2,4,6-tribromophenol, and monobromoacetic esters.

We see what a variety of substances obey the energetic requirements of the multiplet theory. In fact this list must be increased to several hundreds of reactions, since the hydrogenolysis products of the starting materials undergo in turn further hydrogenolysis, which also conforms to the observed rule[6].

The requirements of the multiplet theory are met not only by hydrogenolysis but also by many other reactions investigated. The energy barriers to the types of reactions whose indices are indicated in the lower half of Table 4 have been calculated for nickel from Table 1. The calculated sequence of reactions agrees with experiment. The lower row in Table 4 gives in order of increasing E the reactions — dehydrogenation of hydrocarbons, formation of secondary from primary amines (for example of diphenylamine and ammonia from aniline, where the C–Ni bond is close to =C–Ni), dehydrogenation of amines, dehydration of alcohols, dimerisation of ethylene to butene, migration of the C=C bond in the chain, dehydrogenation of alcohols, and hydrogenation of the C=N bond. The reactions occur in the same sequence with increasing ease on nickel. In conformity with thermodynamics, calculation shows that the difference between E for hydrogenation of an alkene and E for dehydrogenation of the alkane is equal to the heat of hydrogenation ΔH = -30 kcal mole^{-1}.

It must be specially stressed that the values of E for all fourteen indices not containing halogen in Table 4 have been calculated, in agreement with experiment, from only five Q_{AK} values, namely Q_{-CNi}, $Q_{=CNi}$, Q_{NNi}, Q_{HNi}, and Q_{ONi}. This is an indication of far reaching additivity, and confirms Eqns. (1.6) and (1.7).

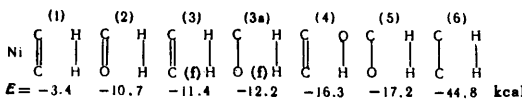
Some of the reactions in Table 4 were predicted in advance, and later carried out experimentally in our laboratory, among them being hydrogenolysis of the N–Br, O–Cl, and O–O bonds (accomplished in the formation of acetamide from *N*-bromoacetamide, of t-butanol from t-butyl chlorite, and of alcohols from peroxides and hydroperoxides), dehydrogenation of amines to aliphatic ketimines, etc.[1]

Hydrogenolysis on Carbon

It was of interest to apply the same method to another catalyst, for which the Q_{AK} values were known. We therefore investigated reactions on carbon between hydrogen and several chlorinated and brominated hydrocarbons[56] and, in greater detail, cyclohexanol[57]. Calculation and experiment showed that, in contrast to nickel, the reaction velocity is controlled by the desorption stage. Calculated and observed reaction sequences showed in general good agreement. The coefficient γ in Eqn. (1.9) should have a lower value with carbon than with nickel. Another difference is that, when a duplet complex is formed on carbon, E must be corrected for the formation of a three-membered carbon ring, in conformity with the fact that the valencies of carbon, but not those of metals, are directional (*cf.* Pauling[58]).

Furan Derivatives[59,60]

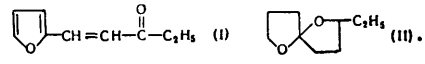
The sequence of reactions involving hydrogenation, cyclisation, and hydrogenolysis of furan derivatives on nickel, predicted from calculations of E based on Table 1, is



(3.2)

where the indices relate to hydrogenation of (1) a C=C bond, (2) a side-chain C=O bond, (3) a C=C bond in the furan ring, and (3a) an ether link in the furan ring, formation of (4) a spiran, and hydrogenolysis of (5) a C–O bond, and (6) a C–C bond. In the hydrogenation of the furan ring it is assumed that the multiplet complex contains half the conjugation energy of furan ($\sigma/2$ = 8 kcal). The volcano-shaped curves are shown in Fig. 5.

As an example, let us consider the reactions of 1-fur--2′-ylpent-1-en-3-one (I)



According to calculation, hydrogenation of (I) over nickel should yield successively — (1) 1-fur-2′-ylpentan-3-one,

‡ Several uncertain names have been translated literally (Ed. of Translation).

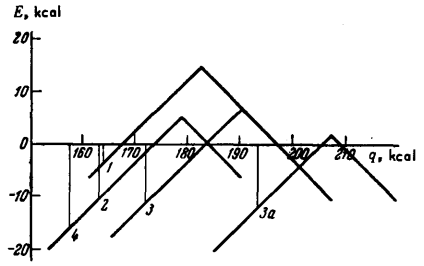
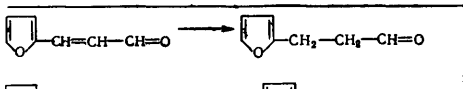
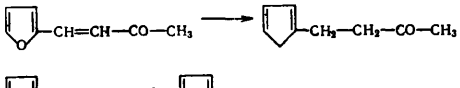
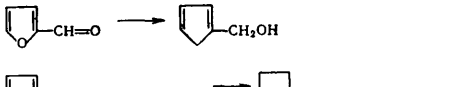
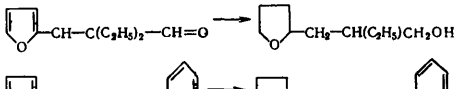
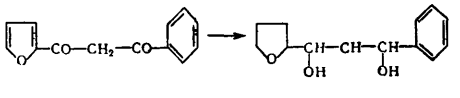
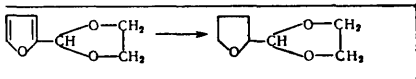
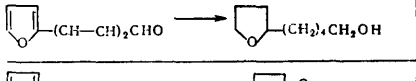
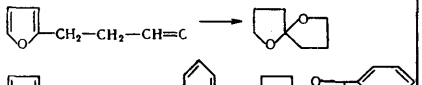
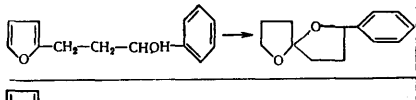
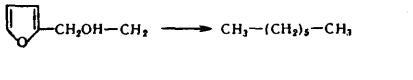


Fig.5. Volcano-shaped curves and heights of energy barriers in the hydrogenation of furan derivatives. Numbering of reactions (1)–(3a) as in Eqn.(3.2).

(2) 1-fur-2′-ylpentan-3-ol, (3) 1-tetrahydrofur-2′-ylpentan-3-ol, and (4) 5-ethyl-2,2′-spirobitetrahydrofuran (II): then, after a series of similar stages involving fission of the ether links, (5) n-nonane, and finally (6) methane.

Some further examples are listed in Table 6. The position of the comma in the column headed *A* in Table 6 indicates between which two successive conversions in Eqn. (3.2) the given reaction halted under the given conditions. This position was found experimentally. An increasing numerical sequence under *A* implies agreement between theory and experiment, as is the case. The higher the temperature the farther to the right is the comma located, which is also consistent with theory.

TABLE 6.

	A	*t*°
	1.236	25
	1.236	
	2.356	90
	23.456	135
	123.456	
	13.56	130
	123.56	
	134.56	140
	134.56	
	12345.6	>300

The theory has been tested on the following§ compounds — β-furylacrolein, furfurylideneacetone, 1-furyl-8-methyl-oct-1-en-3-one, furfurylideneacetofuran, difurfurylideneacetone, vinylfuran, furfuraldehyde, 6-furylhexa-3,5-dien-2-one, 1-furyl-5-methylhex-1-en-3-one, furfurylidenecamphor, 3-furylpropan-1-ol, 3-(5-methylfur-2-yl)propan-1-ol, 4-furylbutan-2-ol, 4-(5-methylfur-2-yl)butan-2-ol, 1-furylpentan-3-ol, 1-furylhexan-3-ol, 1-furylheptan-3-ol, 1-furyloctan-3-ol, 1-furyl-7-methyloctan-3-ol, 3-furyl-1-phenylpropan-1-ol, 1-furyl-5-phenylpentan-3-ol, 3-furyl-2-methyl-1-phenylpropan-1-ol, 3-furylpropionaldehyde, 1,5-difuryl-3-phenylpropane-1,3-dione [*sic*], 1-furylbutane-1,3-dione, furfurylidenebutyraldehyde, difurfurylidenecyclohexanone, 1-furylhex-1-en-3-one, furan, 2-methylfuran, 2-ethylfuran, 2-n-propylfuran, 2-n-pentylfuran, 1-furylbut-1-ene, 2-benzylfuran, 2,5-dimethylfuran, furfuryl alcohol, 1-furylethanol, 1-furylpropanol, 1-furylbutanol, α-furylbenzyl alcohol, 6-furylhexan-2-ol, furfural diethylacetal, 2-furyldioxolan, 2,2′-furoin, 5-hydroxymethylfurfural, 5-furylpenta-2,4-dienal, 6-furylhexa-3,5-dien-2-one, 7-furylhepta-4,6-dien-3-one, 1,9-difurylnona-1,3,6,8-tetraen-5-one, β-furylpropionaldehyde, β-(5-methylfur-2-yl)propionaldehyde, 1,5-difurylpentan-3-ol, tetrahydrofuran, furfurylideneacetophenone, tetrahydro-2-methylfuran, and spirobitetrahydrofuran. Experiment confirmed theory. When both furan and benzene rings are present in a molecule, the former is hydrogenated more readily, in conformity with the requirements of theory, since the resonance energy to be overcome in it is lower (see Section 4). This list has recently been further supplemented by the work of Ponomarev and of Til' [61]. Furan derivatives can be obtained from agricultural waste products, and the above results are of value for exploitation of the latter.

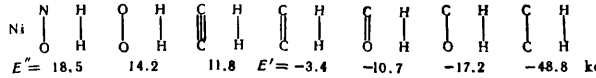
Hydrogenation of Triptycene Derivatives

The Reviewer and Klabunovskii [1,62] investigated the kinetics of the hydrogenation of triptycene derivatives on nickel at 45° and 1 atm. The experimental results were consistent with the calculations of *E*.

Hydrogenation of Peroxides and Hydroperoxides

Interesting results have been obtained [63-67] in a study of the kinetics of the hydrogenation of organic peroxides and hydroperoxides over nickel, palladium, and platinum. Until then almost nothing was known about this class of reactions, and still less about their kinetics.

On the basis of Table 1, the multiplet theory makes the following predictions: (1) peroxide compounds should be readily hydrogenated on nickel, since calculation indicates that the height of the energy barrier is $-E = -14.3$ kcal; (2) the activation energy of such reactions should be close to 7 kcal, from Eqn. (1.9); (3) the rate of hydrogenation should be affected by the structure of the molecules; (4) on hydrogenation over nickel, multifunctional peroxides should undergo, according to Table 1, consecutive reactions in the sequence



(3.3)

§ In view of the uncertainties and inconsistencies of the Russian nomenclature, several names in this list have been left in a semi-trivial form (Ed. of Translation).

(The value 11.8 has been calculated from the data in Table 3); and (5) this sequence may be somewhat different with other catalysts, as follows from Eqns. (1.6) and (1.7).

These expectations have been confirmed by experiment. The reactions already occur at 5–30°, and are of zero or the first order. Some of the results obtained with nickel are indicated in Table 7. The sequence observed with palladium did in fact prove to be different from that with platinum.

The reduction of 2-isopropylanthraquinone with hydrogen over nickel has also been investigated[68], together with the production of hydrogen peroxide when the reaction products oxidise in the air. In agreement with calculation, the C=O bond is reduced sooner than the aromatic ring.

Effect of Substitution within the Indicial Group — General Case[69]

Let one of the atoms, *e.g.* A, in the indicial group (1.5) be replaced by another atom. In order to learn how this affects the energy barrier to the reaction $-E'$, we must examine the variation of E' with respect to A in Eqn. (1.6). Since the remaining quantities are practically independent of A, such variation gives

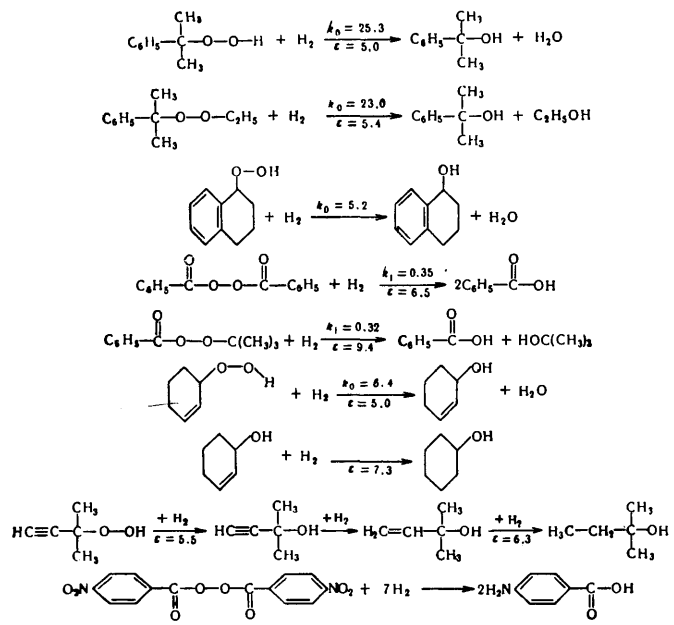
$$\delta E' = -\delta Q_{AB} + \delta Q_{AK} \qquad (3.4)$$

whence

$$\delta E' < 0, \text{ when } \delta Q_{AB} > \delta Q_{AK}. \qquad (3.5)$$

This important relation can be expressed in words as follows: when an atom A in a duplet indicial group is replaced, *i.e.* when $A^1 \rightarrow A^2$, the first of two comparable reactions goes more rapidly than the second ($E_1 > E_2$) if the energy of bonding of atom A with atom B increases more (or decreases less) than the energy of bonding of A with the catalyst K ($Q_{A^2-B} - Q_{A^1-B} > Q_{A^2-K} - Q_{A^1-K}$). Thus on nickel, hydrogenolysis of the Cl–C bond, in which A^1 = Cl, is more rapid than that of the N–C bond, where A^2 = N; and in fact $\delta Q_{AB} = Q_{N-C} - Q_{Cl-C} = 72.8 - 81.0 = -8.2$ is greater (a less negative quantity) than $\delta Q_{AK} = Q_{NNi} - Q_{Cl-N} = 27 - 67 = -40$ kcal (*cf.* Table 4).

TABLE 7.



4. EFFECT OF INTRAINDICIAL SUBSTITUENTS

That part of the multiplet theory which deals with the influence of substituents which are not in contact with the catalyst recalls the theory of colour in organic compounds[70]. The indicial group corresponds to the chromophoric group. The position of the maximum on the volcano-shaped curve along the q axis corresponds to that of the centre of an absorption band in the spectrum, while the influence of extraindicial substituents on E is equivalent to the displacement of an absorption band under the influence of auxochromic groups. Similar views have been expressed by Langenbeck[71].

As a result of the change in electron density, a substituent attached to A, for example, influences the bond energies Q_{AB} and Q_{AK}, and hence also E'. For a quantitative assessment of this effect we again vary Eqn. (1.6) with respect to A. Now, however, A^1 and A^2 denote, not different atoms as above, but the same atom A with different extraindicial substituents. The result of the variation is obviously again conveyed by the formulae (3.4) and (3.5) and by the above verbal formulation, but according to the new definition it is "a substituent attached to an atom A", not the atom itself, which is replaced. The extent to which a substituent influences Q_{AB} has been discussed in Section 2.

Eqn. (3.4) contains the fundamentally important result that in catalytic reactions, unlike non-catalytic reactions, the influence of substituents on reaction velocity and on E must be allowed for twice — on Q_{AB} and Q_{AK} — the two effects being opposed. This explains in particular the apparently contradictory result that in a homologous series the rate in some cases decreases (this occurs when $\delta Q_{AB} > \delta Q_{AK}$), in other cases increases (when $\delta Q_{AB} < \delta Q_{AK}$), and in still other cases remains unchanged (when $\delta Q_{AB} = \delta Q_{AK}$). This last type of behaviour is found in the dehydrogenation of primary alcohols — in the work of Palmer and Constable, Bork and the Reviewer, Lüttich and Briecht¶ (on copper), and especially of Bogdanova, the Reviewer, and Shcheglova (the papers are listed in Ref. 1) — where ϵ remained constant for normal primary alcohols from C_2 to C_9 (on an oxide catalyst). Such cancelling out of the effects of δQ_{AB} and δQ_{AK} is not found in the dehydration of alcohols, and 1-, 2-, and 3-substitution each contributes its own increment to ϵ (according to the work of Dohse and Kölberer¶ on bauxite, of Bork and Tolstopyatova on Al_2O_3, and of the Reviewer, Tolstopyatova, and Stshizhevskii on W_2O_5).[1]

The rate of hydrogenation of alkenes on platinum falls with increasing substitution by alkyl groups of hydrogen atoms adjacent to the double bond (Lebedev's rule[72]). It also falls with increase in the number of phenyl radicals replacing alkyl radicals adjacent to the double bond (Kazanskii and Tatevosyan[73]).

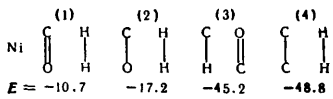
The rate of hydrogenation under pressure decreases on passing from benzene to hexamethylbenzene over Ni on Al_2O_3, but it increases in this sequence over WS_2 (Lozovoi[74,75]).

¶ The spellings of some of the non-Russian names are conjectural (Ed. of Translation).

Chain branching retards the hydrogenation of ketones over platinum (Vavon[76]). A decrease in reaction velocity on substitution implies that $\delta Q_{AB} > \delta Q_{AK}$.

Hydrogenation of Monosaccharides

The multiplet theory has proved useful also in investigating the hydrogenation of monosaccharides[77]. Calculation of E from Table 1 leads us to expect the following reaction sequence



(4.1)

where the indices represent – (1) hydrogenation of the monosaccharide to a polyhydric alcohol, (2) reduction of a hydroxy-group, (3) the Cannizzaro–Tishchenko reaction with formation of gluconic acids, and (4) hydrogenolysis of a C–C bond, for example the formation of glycerol from sorbitol. This sequence is actually observed[77] as the temperature is raised (from 120° to 230° at 150–300 atm). We have made a special investigation of reaction (4).[78,79]

It is especially interesting that it has proved possible[77] also to indicate the effect of extraindicial substituents. As above, let such a substituent be attached to atom A in formula (1.5). By varying the expressions for E' [Eqn. (1.6)] and for u (see Section 1) with respect to A, and using the well-known equation $\Delta F = -u - T\Delta S$, where F is the free energy and S the entropy, we obtain

$$\left.\begin{aligned} \delta E' &= \delta Q_{AK} - \delta Q_{AB} \\ \delta u &= \delta Q_{AD} - \delta Q_{AB} \\ \delta \Delta F &= -\delta u - T\delta\Delta S \end{aligned}\right\}. \qquad (4.2)$$

From the set of equations (4.2) it follows that

$$\delta E' = -\delta\Delta F - (T\delta\Delta S - \delta Q_{AD} + \delta Q_{AK}). \qquad (4.3)$$

For condensed (*i.e.* solid and liquid) systems $\delta\Delta S$ is small, and the difference $\delta Q_{AD} - \delta Q_{AK}$ is also small compared with $\delta\Delta F$. Hence in this case we find from the multiplet theory that

$$\varepsilon E' \simeq -\delta\Delta F, \qquad (4.4)$$

i.e. that when there is no evolution of gas (for example methane), the change $-\delta E'$ in the energy barrier due to substitution should be approximately equal to ΔF. The values of ΔF can be estimated, and Tables 8 and 9 have been compiled on this basis. The δE values in these tables must be added to E in Eqn. (4.1). The values of E themselves do not vary in parallel with ΔF. In agreement with experiment, Tables 8 and 9 show in particular that – (1) C–C and C–O bonds behave differently depending on their position in the molecule; (2) a C–C bond occurring in the middle of a polyhydric alcohol molecule undergoes cleavage most readily; and (3) a C–O bond is more readily broken when attached to primary than to secondary carbon atoms. Some of these generalisations were known earlier[77], but the multiplet theory has provided an explanation of them.

TABLE 8. Hydrogenolysis of polyhydric alcohols at the C–O bond.

Reaction (H_2O formed in each case)	$\delta E = -\delta\Delta F$, kcal
Hexitol → methylpentitol	2.6
Pentitol → methylerythritol	2.6
Erythritol → methylglycerol	2.7
Erythritol → butene-1,2,4-triol	−0.3
Glycerol → propylene glycol	2.1
Glycerol → trimethylene glycol	−1.3
Propylene glycol → n-propanol	−1.6
Propylene glycol → isopropanol	2.5
Ethylene glycol → ethanol	−2.7

TABLE 9. Hydrogenolysis of polyhydric alcohols at a C–C bond.

Reaction	$\delta E = -\delta\Delta F$, kcal
Hexitol → 2 (glycerol)	1.2
Hexitol → erythritol + ethylene glycol	0.4
Hexitol → methanol + pentitol	0.16
Methylpentitol → glycerol + propylene glycol	0.7
Methylpentitol → methylglycerol + ethylene glycol	0.5
Methylpentitol → methylerythritol + methanol	−1.06
Pentitol → ethylene glycol + glycerol	1.10
Pentitol → erythritol + methanol	−0.04
Methylerythritol → ethylene glycol + propylene glycol	0.6
Methylerythritol → ethanol + glycerol	−0.6
Methylerythritol → methanol + methylglycerol	−0.04
Erythritol → 2 (ethylene glycol)	1.2
Erythritol → glycerol + methanol	0.2
Methylglycerol → ethanol + ethylene glycol	−1.2
Methylglycerol → methanol + propylene glycol	0.2
Glycerol → ethylene glycol + methanol	−0.04

Strain in Rings

According to thermochemical calculations[26] Q_{C-C} has values of 73.8, 76.4, 81.7, and 82.9 kcal in the series of cycloalkanes from cyclopropane to cyclohexane. Also $Q_{C_{Ar}-C_{Ar}} = 112.0$ and $Q_{C_{Ar}-C_{Alk}} = 95.2$ kcal. Levi and the Reviewer[80] calculated the comparative ease of closing and opening carbon rings on platinum and on palladium, and obtained results which all agreed with the experimental data of Kazanskii and his coworkers.

Recently Lukina[81] has found a very interesting parallel between the ease of hydrogenation of cyclopropane hydrocarbons and their electronic structure. From the point of view of the multiplet theory this means that the electronic structure influences the Q_{AB} of different bonds in these hydrocarbons, and Q_{AB} is more strongly affected than Q_{AK} in equations of the type (1.6). The cyclopropane ring forms with a double bond a conjugated system, and we thus come up against the problem of the effect of conjugation energy on the rates of catalytic reactions.

Effect of Conjugation Energy

The influence of conjugation energy σ on rate of catalytic hydrogenation has been examined from the standpoint of the multiplet theory[82–85]. When σ is taken into account, Eqn. (1.6) for the hydrogenation of an olefinic bond will be

$$E' = -Q_{C_1=C} - Q_{H-H} + Q_{C_1-K} + Q_{C-K} + 2Q_{H-K} - r\sigma. \qquad (4.5)$$

The appearance of conjugation energy is due to electron delocalisation resulting from interaction of two π-electron systems, and $r \simeq \frac{1}{2}$ is the proportion of σ remaining in the active complex, C_1 being the carbon atom at which the substituent is changed. By varying Eqn. (4.5) we find the effect on E of the nature of the substituent:

$$\delta E = -\delta Q_{C_1=C} + \delta Q_{C-K} - r\delta\sigma, \qquad (4.6)$$

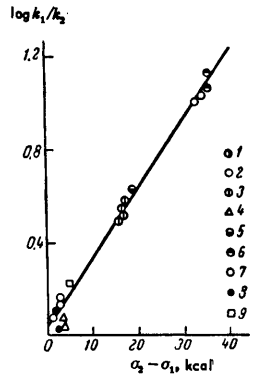


Fig.6. Relation between conjugation energy and rate constant for hydrogenation:
1) cyclopentadiene and benzene;
2) eugenol and *cis*-isoeugenol;
3) dihydrofuran and furan;
4) cyclopentane and cyclopentadiene;
5) furan and benzene;
6) cyclohexa-1,4-diene and benzene;
7) cyclohexa-1,3-diene and benzene;
8) cyclohexa-1,4- and -1,3-dienes;
9) diphenylmethane and biphenyl.

where $\delta Q_{C_1=C}$ and δQ_{C-K} are the changes in the induction and hyperconjugation effects, and $\delta\sigma$ is the change in conjugation energy on substitution. The relation (4.6) is fairly complex in form: in order to find the effect of σ, it is obviously necessary to compare compounds whose structures are such that $\delta Q_{C_1=C}$ and δQ_{C-K} remain as constant as possible. It follows that, under otherwise identical conditions, the disappearance of conjugation energy during a reaction makes hydrogenation more difficult, and similarly its appearance on dehydrogenation should accelerate the latter.

Experiments on the hydrogenation of different compounds under comparable conditions — in solution at 5–60° and 1 atm — over rhodium (0.1–2.5% Rh on Al_2O_3) showed[82] that: (1) an increase in the conjugation energy of the reactant lowers the hydrogenation rate constant k; (2) with small differences in conjugation energy the induction (and hyperconjugation) effects are more strongly developed; and (3) the nature of the solvent has no decisive importance.

A new relation (resembling the Hammett equation) has been discovered[82]

$$\log(k_2/k_1) = a(\sigma_1 - \sigma_2) + b, \qquad (4.7)$$

the subscripts 1 and 2 indicating two different compounds with different conjugation energies, and a and b being constants. The results are illustrated in Fig. 6. The 1,1-diphenyl-2--picrylhydrazyl free radical is difficult[85] to hydrogenate under these conditions; this can be explained by the necessity for overcoming the stabilising effect of the conjugation energy. We have investigated the kinetics of the dehydrogenation of several alkyl–aromatic hydrocarbons (for summary see Ref. 86), and found that, under conditions such that ethylbenzene is readily converted into styrene, ethylcyclohexane remains almost unchanged[87]. This is consistent with what has been said above. The appearance of conjugation energy makes it clear why the dehydrogenation of butane and that of ethylbenzene require different catalysts[88].

The electronic concepts of modern organic chemistry, examples of the application of which have been discussed above, must be expected to prove very useful in developing the multiplet theory: they will be able to explain how bond energies vary, and the latter can be utilised by the multiplet theory.

5. EFFECT OF NATURE OF CATALYST

We have examined above the influence on catalysis of changes in the nature and structure of molecules; in this and the next section we shall consider the analogous effect of changes in the nature of the active centre on the catalyst and in its environment, in accordance with the layer structure proposed for the multiplet complex (see Fig. 3 in Ref. 1).

The Reviewer has suggested[89] that the catalytic properties of elements depend on their position in the Periodic System. Knowledge of the dependence of bond energies between elements and organic radicals Q_{AK} on the position of the former may be expected to be a great help in solving the problem of choice of catalyst. It may be hoped that rules will be discovered which will facilitate the task of selection and eliminate the complications due to method of preparation of catalyst, etc. Then, when a few Q_{AK} values are known, E can be calculated for a larger number of reactions by the method of volcano-shaped curves. The rules which we have already found in this field are given below.

1. Interesting results have been obtained for the rare earths[8], for which Q_{AK} proves to be a periodic function linked with the magnetic moment μ of the ions of the oxides. The values of Q_{HK} and Q_{CK} vary in parallel with μ, while Q_{OK} varies in the opposite sense (Fig. 7). Values of the

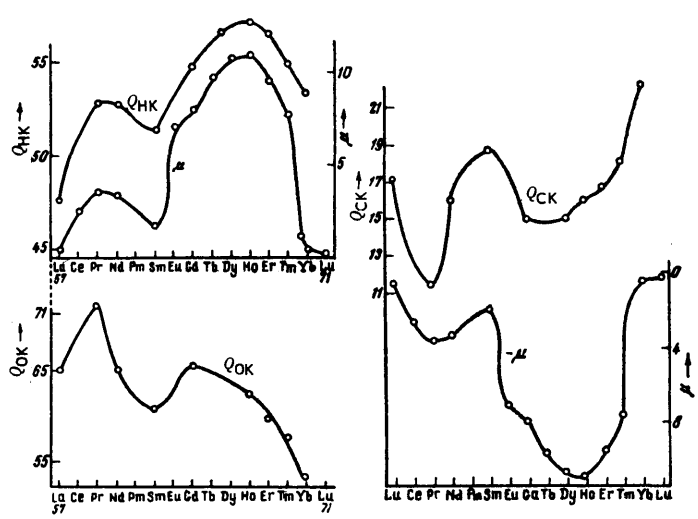


Fig.7. Dependence of bond energies Q_{HK}, Q_{OK}, and Q_{CK} in kcal and of magnetic moment μ in Bohr magnetons on atomic number of rare-earth elements.

activation energy of dehydrogenation of tetralin and alcohols, employed in the calculation of Q_{AK} from Eqns. (2.6)–(2.8), do not vary periodically but monotonically, though irregularly. Hence the Q_{AK} are primary quantities, and the ϵ secondary, in which periodic effects cancel out. This result is important also for electronic theory, since it shows that the inner $4f$ electrons play a part in catalysis (just as they influence other chemical properties).

2. The energy of bonding of oxygen in the reactant molecule with the oxide Q_{OK}^{ki} determined kinetically as a function of the atomic number n varies in parallel with Q_{OM}^{th}, the energy of bonding of the metal with oxygen in the oxide determined by a thermochemical method[42] (see Fig. 8). The Q_{OK}^{ki} are located below and somewhat differently from Q_{OM}^{th} because of the presence of the sublimation term λ (*cf.* Section 6). In Fig. 8 the atomic number n of the element is plotted as abscissa and the corresponding Q_{OK}^{ki} from Table 2 as ordinate. The parallelism between Q_{OK}^{ki} and Q_{OM}^{th} indicates firstly that the former is a periodic function of atomic number, since the latter is such a function; secondly it confirms that in catalysis on oxides the molecules are adsorbed predominantly on the metal atoms, not the oxygen atoms (*cf.* Section 1).

Activation energies have been determined[44] for several reactions on zinc oxide, to whose catalytic properties a combined approach from the viewpoints of the multiplet and the electronic theories was shown to be possible by Dowden *et al.*[90] Values have been found[44] for Q_{HK}, Q_{CK}, and Q_{OK} (see Table 2), and Q_{NK} = 30.8 kcal. Calculation based on these data shows that, in contrast to the situation with nickel, a C=O bond should be hydrogenated on zinc before a C=C bond, and in fact Freidlin and Gorshkov[91] have confirmed this experimentally in several cases.

By means of Eqns. (2.6)–(2.8) it has been possible[92] to use previously known activation energies for the dehydrogenation of alcohols ϵ_2 and their dehydration ϵ_3 to calculate beforehand the sequence of ϵ_1 for the dehydrogenation of hydrocarbons on oxides of metals in Group II of the Periodic System. It follows from these equations that

$$\varepsilon = \frac{2}{3}(\varepsilon_3 + \varepsilon_3) + Q_{OK} - 48.6. \qquad (5.1)$$

Substitution of thermochemical values of Q_{OK} showed that the duplet dehydrogenation of hydrocarbons is impossible on BeO and MgO, can take place with difficulty on ZnO, and is entirely possible on CdO. This theoretical prediction has been confirmed by experiments with cyclohexane, cyclohexene, butene, and ethylbenzene[92,93].

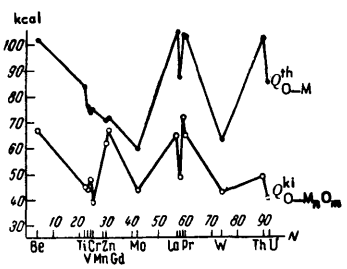


Fig. 8. Parallelism between energy of bonding of oxygen with the surface of an oxide catalyst $Q_{O-M_nO_m}^{ki}$ in kcal determined by a kinetic method and the energy of the metal–oxygen bond in the solid oxide Q_{O-M}^{th} in kcal determined thermochemically from the heat of formation of this oxide from the elements, as functions of atomic number.

Reactions have been studied on the oxides of vanadium, niobium, and tantalum[94–97] and on the oxides and sulphides of molybdenum and tungsten[37,98] in order to determine Q_{AK}.

Eqn. (3.4), which follows from the multiplet theory, explains the reversal of order in catalytic efficiency when one catalyst K_1 is replaced by another K_2: if the term δQ_{AK} predominated with K_1, δQ_{AB} may predominate with K_2, so that $\delta E'$ in Eqn. (3.4) changes sign. This question was discussed in Ref. 69, where a theoretical analysis was given of the change in reactivity when one of the atoms forming the active centre is replaced by another. An attempt has been made to determine Q_{AK} values for Cr_2O_3–Fe_2O_3 mixed catalysts[99].

The work of Jouy and Balaceanu[100] is close in conception to the multiplet theory. These workers used mixed catalysts whose components activated both the O–O and H–H bonds (oxidation) and the C–H and H–H bonds (dehydrogenation), and were able to facilitate the dehydrogenation of cyclohexane and the aromatisation of hept-2-ene and heptane by adding O_2 to them.

6. EFFECT OF ENVIRONMENT OF ACTIVE CENTRE

The activity and the selectivity of a catalyst are affected by the nature, number, and arrangement of its atoms around the active centre. This appears in the influence of the mode of preparation, aging, carriers, etc., and also, in certain cases, of additives.

Let us examine this effect[13,101]. The energy of bonding Q_{A-K} of an atom A with an atom K_1 of the active centre comprises two parts — the energy of bonding with the catalyst lattice Q_{A-K}^0 and the sublimation term λ_A — the latter representing the aggregate effect of atoms adjacent to the active centre:

$$Q_{A-K} = Q_{A-K}^0 + \lambda_A. \qquad (6.1)$$

The quantity λ_A is itself composite. It is demonstrated in the multiplet theory that

$$\lambda_A = \alpha\lambda_K - \lambda_{A-K_1} + \lambda_{A-K_1,K}, \qquad (6.2)$$

where λ_K is the heat of sublimation, *i.e.* the energy of removal of an atom K (see Fig. 9) from inside the catalyst into the gas phase, $\alpha\lambda_K$ is the heat of sublimation of an atom K_1 from the surface (for a smooth surface $\alpha = \frac{1}{2}$ according to Laplace's theorem), λ_{A-K_1} the energy of bonding of the atom A to a surface atom K_1, and $\lambda_{A-K_1,K}$ the energy of bonding of the active complex $A-K_1$ to the surface atom K.

Let us give this proof in brief[101]. When we use a thermochemical method to calculate the bond energy Q_{A-K}^0 from the standard heat of formation of the compound A–K, this relates to the process

$$K(latt.) + A(gas) = A-K(latt.) + Q_{A-K}^0 + \epsilon_0, \qquad (6.3)$$

where ϵ_0 is the energy of electronic excitation. In order to calculate the energy of attraction of an atom A by an active centre of the catalyst K_1, which we denote as the bond energy Q_{A-K_1}, we must examine the process represented by the thermochemical equation

$$K_1(act.\ centre) + A(gas) = A-K_1, K(surf) + Q_{A-K_1} + \epsilon_0. \qquad (6.4)$$

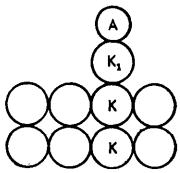


Fig.9. Diagram illustrating physical significance of individual terms in Eqn.(6.2). A fuller explanation will be found in the text.

Let us consider how to pass from Eqn. (6.3) to (6.4). Subtracting the latter from the former, we obtain

$$K(latt.)-K_1(act.\ centre)=A-K(latt.)-A-K_1,\ K(surf)+Q^0_{A-K}-Q_{A-K}. \quad (6.5)$$

Further, we have by definition the following thermochemical equations

$$K(latt.)=K_1(act.\ centre)-\alpha\lambda_K, \quad (6.6)$$

$$A-K(gas)=A-K(latt.)+\lambda_{A-K_1}, \quad (6.7)$$

$$A-K(gas)=A-K_1\ K(surf)+\lambda_{A-K_1,K}. \quad (6.8)$$

It is readily seen from Eqn. (6.6) that the left-hand side of Eqn. (6.5) is equal to $-\alpha\lambda_K$. Subtracting (6.8) from (6.7), we find that

$$A-K(latt.)-A-K_1,\ K(surf.)=-\lambda_{A-K,}+\lambda_{A-K_1,\ K}.$$

Substituting this result in the right-hand side of Eqn. (6.5), we obtain

$$Q_{A-K}=Q^0_{A-K}+\alpha\lambda_K-\lambda_{A-K,}+\lambda_{A-K_1,K}. \quad (6.9)$$

Comparison of Eqns. (6.1) and (6.9) yields (6.2).

Eqn. (6.2) shows that λ_K can be either positive (when $\alpha\lambda_K+\lambda_{A-K_1,K}>\lambda_{A-K_1}$) or negative (when $\alpha\lambda_K+\lambda_{A-K_1,K}<\lambda_{A-K_1}$). In Langmuir's work the adsorbed oxygen film is evaporated from W in the form of WO_3 before the evaporation of O and especially of W, whence $\lambda_W>\lambda_{O-W}>\lambda_{O-W,W}$. This gives an idea of the sequence of λ values.

When $\lambda_{A-K_1,K}$ is small, the multiplet complex may move along the surface[1].

Analogous equations to (6.2) occur also for the bonds B-K, C-K, and D-K. Therefore

$$\begin{aligned} Q_{AK}&=Q^0_{AK}+\lambda_A\\ Q_{BK}&=Q^0_{BK}+\lambda_B\\ &\cdots\cdots\cdots\\ q&=q^0+\lambda \end{aligned} \quad (6.10)$$

i.e. the adsorption potential energy q (which according to the principle of energetic correspondence should be close to $s/2$ for a good catalyst — *cf.* Fig. 2) consists of two parts, q^0 and λ. The controversy between Roginskii[102], who regards supersaturation as the main factor determining the activity of a catalyst, and Boreskov[103], who considers that with the same surface only its chemical nature is significant, comes down to a different relative assessment of q^0 and λ: according to Boreskov q^0 predominates, and according to Roginskii λ. In particular cases the specific catalytic activity may not be affected by microscopic roughness (with sintered catalysts, for example), and λ is then approximately constant, but this cannot be true in general, since the mode of preparation is known to influence the selectivity of catalysis.

If in a given reaction λ for a catalyst prepared in one way is lower than for a catalyst prepared in a different manner, the adsorption potential energy of the first catalyst will be lower than that of the second: $q_1<q_2$.

It follows from condition (1.15) that, if $q_1<s/2$ and if $\Delta\lambda$ is the change in λ on passing from the second to the first catalyst, the reaction velocity will increase when

$$\Delta\lambda<s-2q_1, \quad (6.11)$$

being a maximum when $\Delta\lambda=s/2-q_1$.

When the surface contains a set of active centres having different values of $\Delta\lambda$, but such that the highest adsorption potential energy does not exceed $s/2$, *i.e.* such that $q_1+\Delta\lambda\leqslant s/2$, an increase in adsorption potential energy produces an increase in E and hence in the reaction velocity. This is in agreement with Taylor's views[104]. However, further increase in adsorption, and hence in the adsorption potential energy, now diminishes E' and retards catalysis, in contradiction to his views. Thus catalysis occurs at active centres having some intermediate adsorption potential energy. The maxima on promotion curves may in some cases be due to such an influence of $\Delta\lambda$.

As Sachtler[105] points out, the work function, the Volta potential, the photoelectric emission, emission microscopy, the electrical conductivity of films, the magnetic properties of small particles, and infrared spectra indicate that a chemisorption bond between metal and adsorbate is very similar to the normal bond, their strengths differing by at most 10%. A metal atom involved in chemisorption to some extent loses its metallic properties, with consequent changes in conductivity and intensity of magnetisation. The metal–metal bond is partly ruptured, and a bond is formed with the absorbate, whence follows the ready mobility of the metal atom. All these results are similar to the conclusions of the multiplet theory.

Fig. 3 was first realised in work[106] on Cr_2O_3 catalysts prepared in seven different ways. Differential heating curves and X-ray powder diagrams were recorded for them, and activation energies determined for the dehydrogenation and the dehydration of isopropanol. Volcano-shaped curves were obtained, and values of q determined from ϵ by means of Eqns. (2.5) and (1.11). In agreement

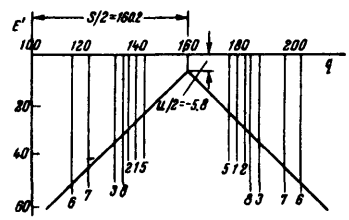


Fig.10. Volcano-shaped curve for dehydration of ethanol on aluminium oxide prepared in different ways[107]. Adsorption potential energies q in kcal and heights of energy barriers $-E$ in kcal; catalyst numbers indicated on vertical lines.

with theory, the observed maximum changes in q (Δq = = 30 kcal mole^{-1}) are less than $\frac{1}{2}\lambda_K$ = 70 kcal mole^{-1} for Cr_2O_3.

Hsi Hsiao-fang and Wu Yüeh[107] applied the method of volcano-shaped curves to the dehydration of ethanol over Al_2O_3 prepared by eight methods. The reaction velocity constants ϵ, E, and q were determined (see Fig. 10, where the Q_{AB} are taken from the scheme in Ref. 23, and the numerals adjacent to the energy barriers denote the catalyst numbers). It is evident that the adsorption potential energy is greatly influenced by the origin of the catalyst, and can fluctuate over the range 25 kcal < $\frac{1}{2}\lambda_K$ [< 55 kcal (Ed. of Translation)] for Al_2O_3.

In agreement with theory, Q_{HK}, Q_{CK}, and Q_{OK} depend appreciably on the method of preparation. This is shown for Cr_2O_3 in Table 10 (abridged from Ref. 30). The bond energies, too, are influenced by different gas pretreatments of the chromium oxide[108,109,33].

Dutch workers have recently published volcano-shaped curves. Fahrenfort *et al.*[110] have made a combined kinetic, infrared, calorimetric, and mass-spectrometric investigation of the decomposition of formic acid on various metals. They conclude that the reaction involves the intermediate formation of an adsorption complex of surface nickel formate type. Comparison of the heat of formation $-\Delta H_f$ of the formate of the corresponding metal with the temperature T_r at which a fixed degree of conversion r is reached ($\log r$ = -0.8) yielded a broken line "resembling Balandin's volcano-shaped curves" (Fig. 11). A catalyst half covered with the adsorption complex is the most active. The reaction investigated by these workers differs from those which we have examined, but it is significant that oxides show the same selectivity towards the decomposition of alcohols and that of formic acid (Mars, Fig. 1 in Ref. 111).

TABLE 10. Effect on Q_{AK} (in kcal) of method of preparation.

Cr_2O_3 catalyst prepared from	Q_{HK}	Q_{CK}	Q_{OK}
$(NH_4)_2CrO_4$	60.8	17.1	45.2
$(NH_4)_2CrO_4$ on asbestos	57.7	23.1	35.1
$Cr(NO_3)_3$, by precipitation with Na_2CO_3	54.7	19.3	71.8
$Cr(NO_3)_3$, by precipitation with Na_2CO_3 on asbestos	60.7	20.2	44.9
$Cr(NO_3)_3$, by precipitation with ammonia	60.9	22.7	51.8

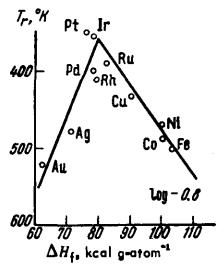


Fig. 11. Volcano-shaped curve[110] for decomposition of formic acid on various metals: $-\Delta H_f$ = heat of formation of metal formate; T_r = = temperature at which 15% conversion is reached.

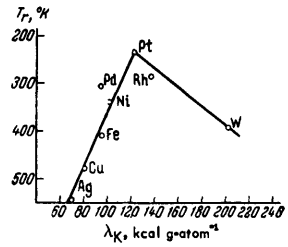


Fig. 12. Volcano-shaped curve[113] for exchange of ammonia with deuterium: λ_K = heat of sublimation of metal in kcal g-atom^{-1}; T_r = temperature at which specified degree of conversion is reached.

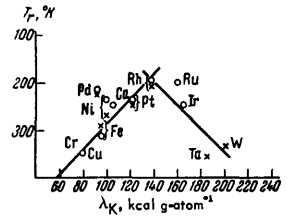


Fig. 13. Volcano-shaped curve[113,115] for hydrogenation of ethylene: λ_K = heat of sublimation of metal in kcal g-atom^{-1}; T_r = temperature at which specified degree of conversion is reached.

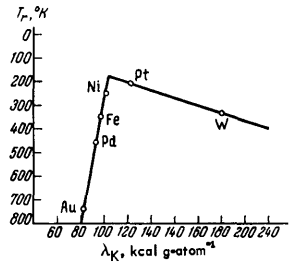


Fig. 14. Volcano-shaped curve[113,117] for hydrogenation of acetone: λ_K = heat of sublimation of metal in kcal g-atom^{-1}; T_r = = temperature at which specified degree of conversion is reached.

In a paper at the Paris Congress on Catalysis, Sachtler and Fahrenfort[112] give additional information on volcano-shaped curves and mention that a similar relation between catalytic activity and the stability of the intermediate complex has been "qualitatively predicted by Balandin".

Schuit *et al.*[113] have computed volcano-shaped curves for still other reactions from results obtained by several workers — deuterium exchange with NH_3 (Fig. 12[114]), hydrogenation of ethylene (Fig. 13[115,116]), and hydrogenation of acetone (Fig. 14[117]). Values of T_r are plotted as ordinates,

and heats of sublimation of the metals λ_K as abscissae. The latter vary in parallel with $q = Q_{AK} + Q_{BK} + \ldots$, which contain λ_K as a component in accordance with Eqns. (6.1) and (6.2). Zelinskii and the Reviewer[118] pointed out long ago the parallelism between the melting points of metals (or λ_K in accordance with Trouton's rule) and the activation energies for the dehydrogenation of cyclic hydrocarbons on them. The T_γ values are inversely proportional to ϵ or E corrected for complicating factors, as a result of which the volcano-shaped curves in Figs. 12–14 are unsymmetrical.

However, changes in λ_K alone are insufficient to explain the position: q contains also the terms Q^0_{AK}, Q^0_{BK}, ... , and graphs having similar volcano shapes are actually obtained[113] if T_γ for the same reactions is plotted against the heat of formation of the corresponding metal oxide Q^I_{OM} or $Q_f(MO)$ in the notation of Ref. 113. Fig. 8 suggests a parallelism between Q^{th}_{OM} and Q^{ki}_{OK}, and Fig. 7 the possibility of a parallelism between Q_{OK} and Q_{HK} (complicated by the mode of production of the catalyst) for the transition metals, too. But Q_{HK} is the predominant term in q for the indices of all three reactions indicated above. This may explain the observed relationships.

It is remarkable that the existence of volcano-shaped curves has received[110,112,113] fresh experimental confirmation of a quantitative character†.

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THE PRINCIPLES OF BIOCATALYST MODELLING

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I. INTRODUCTION

One hundred and thirty years ago a compound was discovered in malt extract that catalysed the conversion of starch to sugar. Payen and Persoz, the discoverers of this natural catalyst, called it "diastase" ("separating"), because it separates dextrin from the starch grain envelope[1]. These workers could never have surmised that it had fallen to them to reach the boundary of a field in which the activity of amazing chemical "machines" is related to life by elusive threads. The increasing attractive force of the problems of enzymology directed the attention of chemists and physicists to this subject, and none of them found in this new and mysterious world anything that could be regarded as trivial from the point of view of their own sciences.

Biocatalysts are products of a long evolution that appears to have extended over several thousand million years. During this time the compounds generally used in technology as catalysts (oxides, salts, sulphides, etc.) were to a large extent deactivated; it is well known that freshly prepared compounds are more active than the naturally occurring forms. Thus, catalytically active systems in the biological field developed in a manner fundamentally different from the evolution typical of inorganic products.

Biocatalysis is one of the facets of life. When it was shown that nearly all chemical processes occurring in cells are catalytic, biocatalysts became particularly important in speculations on the fundamental laws of biochemistry. The development and perfection of forms of life, as well as its origin, have thus been found to be due to the combined action of catalysts. The biological activity of various organisms was a most important channel for the reduction of chemical potentials even in geologically remote times. Therefore, the appearance and development of biocatalysts may be considered as the expression of a general law, according to which potential-equalisation processes in some way set up the mechanisms they require in nature.

In practice circumstances are such that nearly any energy-rich compound formed on the earth as a result of radiation or heating may become the substrate for the nutrition of some organism, heterotrophic or autotrophic. The catalytic systems are found to be unusually versatile. Enzymes, or more accurately aggregates of enzymes, can produce effects that are difficult, and sometimes impossible, to achieve with ordinary catalysts.

Enzymes are virtually the same in both the simplest and most complex organisms, which underlines their versatility as chemical tools. Moreover, the evolution of forms of living organisms has had hardly any effect on the chemical nature of the catalysts required for biological activity.

One of the most striking conclusions that evolutionary biochemistry has led to is that the formation of biochemical systems responsible for metabolic processes was largely completed in remote times[2]. Thus, whatever stimuli acted up to that time ceased, for unknown reasons, to play the part of chemical rearranging factors, as if the function they performed at some stage of development was no longer necessary.

It would be interesting to discover why a certain factor ceased its "creative" activity, and why under certain conditions chemical evolution of the most important catalytic systems was greatly retarded and virtually ceased. Obviously, in our present state of knowledge an answer to this question can be given only in the most general form. If we consider any part whatever of a complex chemical system and examine how the effect of a given chemical factor is reflected in the structure of the chosen part of the system, we observe a number of successive changes in composition and also in macrostructure. The operating factor may be, for example, oxidation by means of hydrogen peroxide, or phosphorylation leading to the formation of pyrophosphate bonds. These factors may cease to operate for two reasons. First, molecules, or groups of molecules, that are unaffected by the given factor, may appear. In this case the resistance may not be constant, since chemical evolution may be resumed as a result of the accumulation of matter. Second, some catalyst may appear in the part of the system under consideration: for example, the oxidative effect and corresponding chemical rearrangement of the system under the influence of hydrogen peroxide became impossible as soon as evolution led to the emergence of catalase. The appearance of enzymes that transfer phosphoric-acid residues, of course, introduce a controlling element into the processes by which phosphoric esters are formed, and so on.

One may imagine a rough sequence in which external chemical attacks lost their random deforming character and, thanks to the development of catalytic systems, became trigger systems for coordinated processes, maintained by the same catalysts.

Processes associated with the transfer of energy-rich groups, and also hydrogen-transfer processes, are probably among the oldest, that is, the earliest to be subjected to control. Much later, processes in which molecular oxygen took part were subjected to control and ceased their deformative activity. This also appears to apply to photosynthetic processes. Kamen[3] points out that anaerobes

which synthesise chlorophyll, differing from that required for the photosynthetic formation of oxygen, cannot exist in an atmosphere containing even traces of oxygen. All living organisms were once anaerobes. Different forms of these organisms that had a photosynthetic apparatus disposed of a catalyst system very similar to that which provides for the respiration of aerobes; the absence of cytochrome oxidase, which is characteristic of anaerobes, evidently plays an important part in their fate.

The macromolecular masses of proteins and the complex structure of the active centre of proteolytic enzymes suggest that these catalytic systems arose much later. All these conjectures are doubtless very debatable; however, it seems useful to look for a relation between the causes that led to cessation of the chemical rearrangement of cellular matter and the action of biocatalytic systems. The main difficulty is that internal as well as external factors must be taken into account in its analysis. It would therefore perhaps be more correct to seek a solution of similar problems in model structures.

However, the cessation of activity of a given external chemical factor as a result of catalyst formation is, of course, by itself insufficient to explain important facets of the activity of catalyst systems in nature; in particular it does not supply an interpretation of the development process.

If we wish to understand the significance of the laws to which the development of biocatalytic systems is subject, we may assume that these laws also manifest themselves in structures much less complex than the living organism. This consideration leads to the problem of modelling both the individual centres of biochemical "machines" and the catalytic systems as a whole.

To-day the term "modelling" is probably much more common than in any other epoch of scientific development. It is striking that modelling has become the subject of research, on the one hand, by biochemists comparing the chemical nature of enzymes with less complex compounds, and on the other, by physicists and engineers interested in the problems of cybernetics. The young branch of science, bionics, is concerned with the setting up of mechanisms that reproduce communication systems in complex aggregates of cells. The chemist turns his attention mainly to molecules, within which he hopes to find keys to the secret behaviour of cellular material, but the engineer, assembling relays and other components that simulate the functions of neurons, has little interest in the material they are made of. However, this separation of points of view can only be temporary.

In fact, the course of biochemical evolution has led to the formation of systems in which their "material" satisfies the demands of further development in the best possible way. This development is no longer related to significant rearrangement of molecules of the material; purely chemical evolution, as has been noted, was largely completed a very long time ago. Since that time, the course of development of more and more complex forms of life actually began to resemble the combination of manufactured relays in the hands of the "constructor". However, if we confine ourselves, on the one hand, to copying communication systems of organisms, and on the other, to models of individual enzymes, we shall lose sight of the necessity of investigating the law by which this "independence of the material" arises.

The question of modelling the process of self-reproduction has been considered by Neyman, Penrose, and Krol'[4]. In all cases the "medium" consisted of radio components, which replaced the nutrient medium of organisms and served as the raw material for self-organising machines. Krol' has noted that, since such artificial media do not exist in nature, we are not witnessing the evolution of machines, not having prepared the necessary media artificially. This observation is extremely characteristic; it indicates a situation in which the problem is being solved "from both ends". Clearly, the problem at the "junction" of two approaches — at the molecular and machine levels — is more complicated; it is also of exceptional interest.

The independence of the material probably becomes much more obvious when we are concerned with the higher functions of complex organisms of the same species. If the identity of the reactions on which phenomena such as muscular work in man and luminescence in insects are based is surprising, still more striking is the unusual diversity of forms of psychic activity in man, that is, of systems the chemical energetics and other properties of which are profoundly similar.

Investigation of the role of chemical structures in organisms shows that we are concerned with initial compounds that are capable of forming more highly ordered structures with a higher degree of organisation, entirely new properties, and unusual stability. But they themselves are not static; they arise and disintegrate in such a way that their appearance and disappearance are really forms of a process, or aggregate of processes, linked to the medium by feedback mechanisms. The most important condition for their existence is the wonderfully coordinated work of the catalytic systems of the very enzyme models which attract increasing attention every year. It must be emphasised that a study of enzyme models cannot be separated from the general problem of biochemical evolution.

II. SHORT HISTORICAL SURVEY

The problem of biocatalyst or enzyme modelling has a history of half a century. In the first attempts to reproduce the functions of enzymes the main effort was directed towards obtaining high activity, since this facet of enzyme action was particularly attractive to chemists.

In this period experiments were done with colloidal metals such as platinum, palladium, and others. Metal sols prepared by Paal and Skita at the beginning of the century showed high catalytic activity in a number of reactions, particularly in hydrogenations[5-7]. Experiments by Bredig and others showed that in some respects, such as high activity and sensitivity to poisoning, metal sols actually resemble enzymes. However, because of the great difference in chemical nature between a metal and the protein of an enzyme, sols cannot be regarded as biocatalyst models. In 1908 Bredig and Fajans found that nicotine has catalytic properties: it separates the optical isomers of the camphoric acids[8].

The work of Hofmann and Gotlob on organic vulcanisation accelerators[9] was done in 1912. In 1926 the first step was taken towards investigating the activity of groups characteristic of enzymes. Kuhn and Brann studied the dependence of the catalytic activity of iron on bond type; they examined haemin, an organic complex of iron with the protoporphyrin nucleus. Compounds of this type form the active groups of a large num-

ber of enzymes that catalyse oxidative processes; the properties of haemin were therefore important in modelling. In enzymes haemin is bound to the protein, and the measurements of the activity of isolated haemin to some degree threw light on the part played by proteins in biological catalysts [10].

The catalytic activity of haemin is dealt with in a fairly large number of papers [11]. Haemin is an active catalyst in the decomposition of hydrogen peroxide and in some oxidations. However, it was clearly shown in experiments on these reactions that the active group is much less active and not quite as selective when it is isolated from its carrier. The activity of haemin in the hydrogen peroxide decomposition reaction is increased by adsorption on charcoal; adsorption activates haemin in some, but not all, reactions in which it generally behaves as a catalyst.

Simple iron ions are also activated by adsorption on charcoal. Such systems may be regarded as the simplest, and very rough, enzyme models in which the active group and the carrier are both represented.

According to Warburg [12,13], iron-containing charcoal, produced by the charring of haemin, shows considerable activity in the oxidation of amino-acids. Examination of its magnetic properties and X-ray analysis led us to conclude that this charcoal contains complex organic compounds of iron and nitrogen firmly adsorbed on the charcoal [14].

In 1926 Kuhn and Brann noted the marked peroxidase activity of iron complexes [10]. A year earlier Baudisch studied the properties of a catalyst consisting of the sodium salt of a pentacyanoferrate(III) and found that this compound accelerated the oxidation by hydrogen peroxide of a mixture of phenylenediamine and benzidine [15].

In 1929 Euler and Jansson [16] showed that complexes of copper with hydroxy- and amino-acids are almost inactive in the hydrogen peroxide decomposition, but complexes with pyridine and ammonia are active. Probably because they used dilute solutions, these workers obtained an incorrect value for the activity of the pyridine complex; it is at least 15 times as active as indicated in their paper.

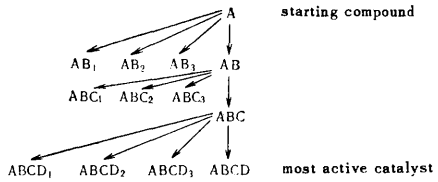
The study by Manchit and Pelann [17] of the $\alpha\alpha$-dipyridyl iron complex has attracted great attention. The catalase function of this complex does not appear to be related to a change in the ionic charge of the bivalent iron; the complex containing one or two dipyridyl molecules per iron ion is active.

In 1932 the work of Bredig and Gerstner on "faser--catalysts" appeared; these consisted of cellulose chemically bonded to diethylamine. The amine played the part of an active group and the cellulose that of a carrier. Faser-catalysts, which Langenbeck considers to be the first enzyme models, accelerated the elimination of carbon dioxide from bromocamphoric acid and showed signs of optical selectivity [18].

Shibata and coworkers studied the stereochemical selectivity of the optically active cobalt complexes. In particular, it was found that *d*-catechin is more rapidly oxidised under the influence of the *d*-forms of cobalt complexes [19,20].

The work of Langenbeck [21], who developed and applied the principle of "systematic activation" in studies on organic catalysts for certain reactions, is particularly interesting. The basis of the principle is that active compounds, selected from those that accelerate a given reaction, are modified chemically by the addition or substitution of new groups. From the derivatives thus obtained, the most active are selected and further modified by substitution. In this way Langenbeck achieved great success; he gradually increased the activity of catalysts for the decarboxylation reaction, until the best model was less active than the natural enzyme only by a power of ten. The initial link in the catalyst chain was methylamine, which is fairly weak, and the final link 1-methyl-3-aminooxindole. Phenylglyoxalic acid was used as a substrate.

The general scheme of Langenbeck's method may be briefly represented as follows:



Langenbeck also obtained a heterogeneous model of carboxylase, using methyl salicylate and lecithin as carriers; these dissolved the catalysts and formed an emulsion in aqueous solution.

The method of increasing the complexity of the molecule by replacing certain atoms in the organic catalyst by radicals also proved fruitful with the iron-porphyrin complex. Langenbeck showed that the addition of imidazole or its derivatives to haemin sharply increased its catalytic activity in the hydrogen peroxide decomposition, and in the oxidation of pyrogallol and cysteine.

In his study of dehydrogenase models, Langenbeck, using previous observations of Traube, found that isatin may be regarded as a model for amino-acid dehydrogenase. It is interesting that hydrogen given off by an amino-acid may be transferred not only to oxygen but also to another acceptor, for example, Methylene Blue.

The active groups of many important enzymes contain a metal in the form of a complex. It is therefore quite natural that the problems of modelling should include the examination of the possibility of using complexes as catalysts. However, the problem proved to be more complicated than might be expected from analyses of catalase and oxidases of different types. A large number of metals are essential for the functioning of biocatalytic systems; the mode of action of cations is often obscure, although there is no doubt about the presence of a given cation ("activator") in the catalytic system.

It has been established that in living organisms a deficiency of ions of one metal may be made up by the presence of an excess of ions of another.

Recently, Hewitt [22] published a review of the metabolism of microelements in plants. Calcium in plant cells may be partially or wholly replaced by strontium, molybdenum by tungsten or vanadium, potassium by rubidium, and so on. This is doubtless related to the activation of different enzymes by metal ions. Undoubtedly, a large number of enzymes, the active groups of which do not contain metals, show activity in the presence of metal ion activators.

Activation by metal ions is much less specific than the function of ions that form complex catalysts of constant composition. Thus the enzyme tyrosinase is activated by iron, cobalt, and manganese ions; leucineaminopeptidase

is activated by magnesium and by manganese; arginase by manganese, cobalt, nickel, and iron; and carboxylase by manganese, cadmium, zinc, lead, nickel, iron, magnesium, barium, and copper. Activators of some types of phosphates are equally numerous.

Thus, the catalytic functions of transition metal ions are fairly clearly divided into two groups with different mechanisms of action.

The first group comprises cases of catalytic activity in which the metal forms definite compounds with closely limited functions. It includes, of course, such complexes as catalase, peroxidase, and other haemin enzymes, and vitamin B_{12}, a cobalt complex. As a rule, in this group one metal cannot be replaced by another without profoundly changing the catalytic properties.

Processes in which metal ions are only activators must be assigned to the second group. The basic features of this division is that ions of the first group are "non-replaceable", and therefore the mechanisms of action in both groups cannot be entirely identical. Although many properties of individual complexes of the first type have been thoroughly investigated, the mechanism of action of most activators is unknown and sometimes appears quite puzzling[23,24,25].

A particularly important type of active combination with a metal ion is one in which increased activity of the ion is achieved by means of certain ligands bonded to it, which are not substrates for the reaction; the metal porphyrins are a classical example of such complexes. The ammine complexes of copper and some complexes of iron, cobalt, and other metals show high activity in oxidation–reduction reactions.

A still more complicated system is that in which high activity is achieved by bonding of the metal–ligand complex to a protein carrier. Representatives of this class include enzymes and some enzyme models. A well-known review[26] of this problem published by Schwab and Rost about a quarter of a century ago gives information on model catalysts; the authors did not separate models simulating the active group proper from those that included a high-molecular-weight carrier. The models were divided into five groups. To the first the authors assigned "inorganic enzymes", that is, colloidal metal hydroxides and hydroxides having hydrolase (phosphatase) functions. The second group included the "respiratory models" of Warburg and Krause, that is, charcoal and a mixture of hydroxides of transition metals. This was followed by organic bases and the complex catalysts (compounds of cobalt) studied by Shibata. The fourth group included catalysts of the metal–quartz type and faser-catalysts. The fifth group included haemin and Langenbeck's "main valency" catalysts.

III. SOME MODELS OF IMPORTANT ENZYMES

At the present time the number of model catalysts has increased and the progress of knowledge in the field of enzymology has enabled us to find criteria better than activities for assigning a given catalyst to the class of "models". Obviously, metal sols and quartz cannot be regarded as models. Similarity of the model's general type of chemical structure to that of the true active centre of the enzyme is gradually becoming the starting point for researches in this field.

In a paper presented at the Fifth International Biochemical Congress, Westheimer pointed out the successes in the field of modelling that have led to the setting up of catalytic systems that operate under conditions close to those existing in cells by mechanisms similar to those of enzymes. He was confident that we shall soon be able to consider analogues of enzymes as well as models[27]. It was made clear that the mechanism of action of enzymes shows some distinctive features for which we cannot find analogies in ordinary catalysis. For this reason, it would be more rational to model the catalysis itself in the highly organised systems in which enzymes operate rather than the catalysts.

As for the individual compounds having similarities in structure and activity to enzymes or their cofactors, without exhausting the whole literature on the subject, several typical models of the most important enzymes will be mentioned. Oxidation–reduction enzymes have been modelled very frequently; catalase, the active group of which is a metal porphyrin, has been a favourite object for modelling; models of its active group have been sought amongst complexes of various metals.

In the author's laboratory[28-31] investigations have been made of the catalytic activity of complexes of copper, iron, cobalt, nickel, zinc, lead, and other metals in the hydrogen peroxide decomposition reaction, and in the oxidation of polyphenols, benzaldehyde, phenylenediamine, ascorbic acid, hydrogen sulphide, and other substrates. Compounds of copper have been studied in particular detail, since the catalytic function of the copper ion can be enhanced about a millionfold by complex formation with ammonia or amines. The complexes may therefore be regarded as "copper" models of catalase. By varying the ligand, we can find how such factors as chelate formation, substitution of other atoms, in the coordination sphere instead of nitrogen atoms, pH, complex stability, etc. affect the catalytic activity. For most of the complexes we studied, the order of reaction with respect to hydrogen peroxide was close to unity, that is, the picture as a whole is very similar to that observed with ammines.

The presence of a maximum on the curve showing the dependence of activity on the concentration of the free ligand in solution is a regular feature. The concentrations of amino-compounds corresponding to the activity maxima depend, of course, on the nature of the amine; sometimes they are fairly high[32]. This is due to the formation of more or less unstable six-coordinated complexes in the presence of an excess of ligand. Free positions in the coordination sphere are essential for catalysis. In practice the activity can often be conveniently evaluated as the number of moles of hydrogen peroxide decomposed per minute in the initial period of the reaction (for example, in the first five or ten minutes), calculated per gramme-ion of copper. If the plot of the amount decomposed against time departs appreciably from linearity, the slope at the origin is found by extrapolation. It is useful to maintain the amine concentration at a level corresponding to maximum activity. From the results of experiments with different buffers, a correction for pH can be introduced, and the activity can then be expressed at a single pH. Table 1 lists the most characteristic models of catalase. The activity of some of these is lower than that of the enzymes by only one or two powers of ten. It should be remembered that catalase is quite exceptional as a biocatalyst; for this reason, the setting up of such working models is of interest from the point of view of the theory of catalysis, irrespective of the problem of modelling.

TABLE 1. Some catalase models containing metal.*

Metal ion	Ligand	Activity	Literature references
Cu^{II}	amino-acids, piperidine, peptides, proteins	weak	28, 32, 33
Fe^{III}	salicylic acid	weak	34
Cu^{II}	amides, amino-alcohols, pyridine, picoline	average	28, 35
Fe^{III}	haem, its derivatives, phenanthroline, phthalocyanine	average	21, 36
Cd^{II}, Zn^{II}, Pb^{II}, Fe^{III}, Co^{II}	Schiff bases	average and weak	37, 38
Cu^{II}	ammonia, amines, diamines *N*-substituted diamines, biuret	high	28, 30
Fe^{III}	triethylaminotetramine	high	39

* The activity of a catalyst is termed "weak" if it is close to unity, "average" if it is ~ 10, and "high" if it is greater than 100.

It is interesting that piperidine complexes show low activity (1.2); this indicates the importance of amine nitrogen for the catalase function of the complex.

The catalytic functions of complexes formed by transition metal ions with biuret, triuret, peptides, and proteins[37] deserve mention. Biuret complexes show the highest activity at the limit of their decomposition; if the concentration of biuret in the solution is raised so as to make the complex stable, the activity falls sharply[34].

The author has studied the decomposition of hydrogen peroxide by a biuret complex at different temperatures. The temperature coefficient of the reaction is very low; the activation energy is 1500–2000 kcal mole^{-1}. Here the high catalase activity is associated with a low activation energy. The biuret complex is more active than the copper ammines and is undoubtedly a powerful catalase catalyst.

Although weak, the activity of protein–biuret complexes depends on the nature of the protein. Globulins form the most active complexes, followed by gelatin, casein, and albumin.

We shall now consider the catalytic properties of iron complexes, and, to begin with, we should emphasise that the iron–porphyrin complexes, which form the active part of a number of oxidative enzymes and electron carriers, may show considerable activity even when isolated from the protein carrier. The activity of these complexes is increased by the addition of some compounds, including pyridine and imidazole and its derivatives, which greatly increase the activity of haem. It is particularly interesting that if we select different derivatives of imidazole, we can alter the specific catalytic action: the compound of haem with sodium imidazole-4,5-disulphonate has pronounced peroxidase properties but does not catalyse the decomposition of hydrogen peroxide. Compounds of haem with imidazole, on the other hand, are four times more active in this reaction than haem itself[21]. Similar compounds may evidently be formed in organisms and perform definite biological functions; they may nevertheless be regarded as models, since the selectivity is controlled not by the protein part of the catalyst but by a much simpler group.

The introduction of ammine nitrogen into the coordination sphere of the complex activates the catalase function of the iron ion. When solutions of sodium nitroprusside are treated with ammonia the compound $Na_3[Fe(CN)_5NH_3]$ is obtained. The author has compared the catalytic activity of solutions of potassium ferrocyanide, nitroprusside, and this ammonia complex. The hexacyano-complex and nitroprusside show very low activity, but the introduction of ammonia sharply increases the catalytic activity; exactly the same effect is observed as that which was so clearly established in the discussion of copper complexes.

Complexes of metals with Schiff bases, especially those obtained from *o*-aminophenol and salicylaldehyde (SAP), are of interest, because, although they are unstable to hydrogen peroxide, in non-aqueous solutions and mixtures they give rise to effects that cannot be observed in purely aqueous solutions.

Kudryavtsev, Savich, Kundo, and Nikolaev studied the decomposition of hydrogen peroxide in water and in borate buffer. At pH 6–7 in aqueous solution only the compounds of cobalt, copper, and nickel were active; other ions do not form active complexes with SAP. In borate buffer at pH 9.8 all the ions showed much greater activity; the order of increasing activity was different: nickel, cadmium, copper, zinc, lead, iron, cobalt; the activity of the cobalt complex was increased by a factor of 3, and the activity of the iron compounds was sharply increased[37,38,40].

The activity of the zinc compounds in particularly interesting: the zinc ion shows practically no catalase activity. Here the change from the ion to the complex gives rise to a qualitatively new catalytic function.

Still more striking results are observed in pyridine solutions. The catalase activity of lead ions in the form of a complex with SAP increases nearly 300 times (calculated on the metal) compared with the activity of the simple ion. The same order of activation is observed with iron, cobalt, and nickel. The latter is noteworthy since the nickel ion and many of its complexes are virtually devoid of catalytic activity. The following is the order in which the activity increases in pyridine–water (1 : 9) mixtures: zinc, cadmium, copper, nickel, cobalt, iron, and lead. From a comparison of data on ligand structure with the activity of different complexes, more or less general conclusions can be drawn, at least for aqueous solutions. Catalytic activity is favoured by the presence of amino--nitrogen in the coordination sphere, particularly by the presence of four nitrogen atoms and a chelate structure. Calculations of the electron density distribution made for several active copper complexes by Goudot[41] showed that high activity corresponds to the presence of a negative charge on the copper ion, that is, there is a marked donor effect.

The catalase activity is reduced if oxygen enters the coordination sphere or if a saturated coordination complex is obtained. Compounds with high activity usually show relatively low complex stability.

The author's results indicate that a radical mechanism is unlikely for the decomposition of hydrogen peroxide by these complexes. There are grounds for believing that the complexes form intermediate products containing HO_2^- and H_2O_2. In most cases these products form loose transition

states, and the kinetic equations contain large entropy factors and comparatively large activation energies. However, this is not a general rule; some complexes, for example Cu-biuret, are characterised by low activation energies.

The oxidase functions of complexes present a picture of greater diversity than the catalase functions, although usually such a sharp increase in activity on complex formation is not observed as occurred, for example, with the copper ion. In oxidation reactions catalysed by metal ions complex formation, in particular chelate formation, may reduce the characteristic catalytic activity of the ion. A similar phenomenon usually occurs when the ion combines with ligands to give stable complexes[46].

Chalk and Smith[42] showed that copper, manganese, and iron ions accelerate the oxidation of cyclohexene, copper by a factor of ~100, iron by a factor of 10, and manganese by a factor of 200. Bonding with disalicylideneethylenediamine increased the activity of the iron by a factor of ~40; it also increased the activity of manganese slightly but reduced that of copper by a factor of ~10. This example is characteristic in that it shows how specific is the action of a given ligand on the quantitative and qualitative catalytic functions of the ion. Thuillier points out the obvious similarity of the structure of the iron–EDTA complex to that of cytochrome[49].

A similar example is to be found in the phthalocyanines. Structurally, the phthalocyanines are very similar to the porphyrins; for this reason, a comparison of the catalytic properties of the metal complexes of both types of compound is of interest. Sodium, potassium, calcium, barium, and cadmium phthalocyanines show the properties of salts, but the derivatives of other metals are complexes. In 1938 Cook[36] studied the catalytic properties of complex phthalocyanines of different metals in the decomposition of hydrogen peroxide and in oxidation reactions. Phthalocyanines are very insoluble in water; Cook therefore dissolved them in 75% pyridine, and in some cases even in concentrated sulphuric acid.

Cook examined the catalase properties of iron, zinc, chromium, and vanadium. Compounds of bivalent iron showed the greatest activity. In addition to studying the homogeneous decomposition of hydrogen peroxide, Cook attempted to compare the properties of haemin with those of the phthalocyanine complexes; he deposited the phthalocyanine compounds on wood charcoal. The activity of haemin was greatly increased by adsorption on charcoal, and iron phthalocyanine showed a similar effect. The adsorbed catalyst could be poisoned by cyanides.

Cook investigated the oxidation of organic compounds by atmospheric oxygen catalysed by metal phthalocyanines; the iron compound was found to be active, functioning as an oxygen carrier. Because of the poor solubility of the complex, the catalysis was heterogeneous in most experiments. Moreover, in some oxidations considerable decomposition of the complex occurred.

Paquot[50] used phthalocyanine complexes to accelerate the atmospheric oxidation of olefinic hydrocarbons.

Myer[46] showed that the formation of complexes with diamines increased the catalytic activity of iron ions by 300% and of manganese ions by 480% in the oxidation of linseed oil; it is interesting that complex formation with these ligands had practically no effect on the catalytic activity of the cobalt ion. With manganese the activating ligand was disalicylideneethylenediamine and with iron, *o*-phenanthroline. The formation of a five- or six-membered ring, with the metal ion bonded to nitrogen, is important for activity.

Copper ions catalyse the oxidation of the most diverse compounds, including ascorbic acid, hydroquinone, cysteine, glutathione, etc. The author has found that some compounds to some extent enhance the oxidative function of copper; the activator–copper–substrate complex is oxidised more rapidly than the copper–substrate complex. Histidine activates the oxidase function, possessing a weak but well-marked activating effect on the copper ion[43]. The copper–histidine complex was found to be inactive in the oxidation of pyrogallol.

A study of models of the enzymes that oxidise polyphenols is of considerable interest. The classical investigations of Bakh led to the conclusion that the enzyme that oxidises pyrogallol contains copper. Korpusova and Nikolaev[47] studied various complexes of the copper ion from the point of view of their ability to accelerate the oxidation of pyrogallol solutions with gaseous oxygen. It was shown that in many cases the formation of complexes greatly enhanced the catalytic activity of the copper ion. The monoethanolamine and ethylenediamine complexes were the most active compounds, but the isopropanolamine and propylenediamine complexes were also very active.

It is particularly interesting that the amines themselves show appreciable catalytic activity. This effect may be explained on the assumption that a hydrogen bond is formed between the hydroxyl hydrogen and the amine group, which facilitates the oxidation. In aqueous solution the water molecules and the pyrogallol compete for the electron pairs of the amine nitrogen atoms. It therefore follows that the stronger the bond between the hydroxyl hydrogen and the amine the more active will be the corresponding amine.

TABLE 2. Models of various oxidases and peroxidase.

Metal ion	Ligand	Reaction	Literature references
Mn Fe^{II}	disalicylideneethylenediamine	oxidation of cyclohexene	42
Fe^{II}	catechol	oxidation of ascorbic acid	43
Fe^{II}	antipyrinetoluenesulphonic acid	oxidation of ascorbic acid	43
Fe^{II}	sodium nitroprusside	oxidation of pyrogallol	44
Fe^{II}	EDTA	oxidation of tetralin, octalin, pinene, methylcyclohexene, pyrogallol, benzaldehyde, olefins, etc.	45
Cu^{II}	histidine, insulin	oxidation of ascorbic acid	43
Mn^{II}	disalicylideneethylenediamine	oxidation of linseed oil	46
Cu^{II}	amino-alcohols, pyridine, ethylenediamine, propylenediamine, morpholine	oxidation of pyrogallol	47, 48
Cu^{II}, Co^{III}, Ni^{II}	Schiff base	oxidation of ascorbic acid and pyrogallol	40
Co^{III}	ethylenediamine, ammonia, chlorine	oxidation of catechin	19

Thus, if the reaction between a proton and the amine is represented by the equation:

$$HAm^+ \rightleftarrows H^+ + Am,$$

where HAm^+ is the protonated form of the amine, then the lower the equilibrium constant of this reaction (*i.e.* the higher the concentration of the protonated form of the amine) the greater is the activity of the amine. Table 3 shows that there is a strong correlation between the equilibrium constants and the activities of different amines.

Comparison of the activities of these ligands with those of the complexes shows that the increase in activity due to complex formation depends on the nature of the amine; with mono- and di-ethanolamine the increase is well marked, but the activities of ethylenediamine and propylenediamine are virtually unchanged by complex formation.

Thus, the inclusion of a metal in the unstable amine–polyphenol system does not increase the rate of oxidation in all cases, but, as far as can be judged from limited results, only when the amine does not form a chelate structure. In experiments with different amines the author showed that the difference in entropy between the catalysed and uncatalysed reactions depends on the nature of the amine; the sign as well as the magnitude of the difference changes. This difference is positive for isopropanolamine and monoethanolamine, and the entropy of the transition complex containing the catalyst is larger than that of the transition complex in the normal reaction. On the other hand, catalysts containing picolines as ligands give rise to a transition complex with reduced entropy, and acceleration of the reaction is associated with a fall in activation energy.

The catalytic activity of complexes of copper with morpholine in reactions of diphenol compounds has been studied by Brackman and Havinga. They proposed a reaction scheme in which conversion of quinones[48] played an essential part. These workers also found that the activity of copper is increased by complex formation. Many complexes with Schiff bases show catalytic activity. In 1956 Langenbeck and Koechler[37] described the catalytic properties of complexes with Schiff bases prepared from sulphosalicylic aldehyde. Parallel studies were done on chelates formed from pyridoxal, the structure of which is somewhat similar to salicylaldehyde. Both types of chelates showed activity in the oxidation of pyrogallol and purpurogallin; cobalt chelates are very active. The Schiff base prepared from salicylaldehyde increased the activity of the cobalt ion 10 000 times, and that prepared from pyridoxal increased it 1000 times.

TABLE 3.

Amine	Activity, $cm^3 O_2/3$ min	$K = \frac{[H^+][Am]}{[HAm^+]}$
Pyridine	0.8	$1.6 \cdot 10^{-6}$
Triethanolamine	1.1	$1.2 \cdot 10^{-8}$
Diethanolamine	1.4	$1.1 \cdot 10^{-10}$
Monoethanolamine	3.2	$2.5 \cdot 10^{-10}$
Propylenediamine	8.5	$1.1 \cdot 10^{-10}$
Ethylenediamine	9.5	$3.0 \cdot 10^{-10}$

TABLE 4. Some hydrolase models.

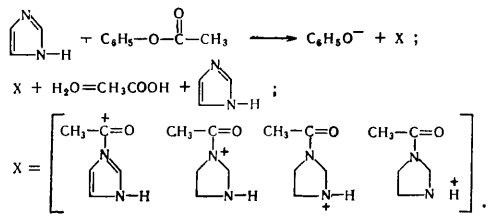
Compound	Reaction	Literature references
Complexes:		
Copper with ligands: ethylenediamine, dipyridyl, histidine, phenanthroline, imidazole	hydrolysis of diisopropyl fluorophosphate	52
Imidazole and its derivatives	hydrolysis of phenyl acetate	53

Kudryavtsev *et al.* have shown[40] that complexes of copper, cobalt, and nickel with Schiff bases prepared from salicylaldehyde and *o*-aminophenol (SAP) have an appreciable oxidase activity. In studies on the dependence of the catalytic functions of complexes of this type on the nature of the metal, aqueous and aqueous pyridine solutions of cobalt, copper, nickel, zinc, cadmium, lead, and iron complexes were examined. The high activity of the complex containing copper is noteworthy; this is a specific catalyst in the oxidation of ascorbic acid. Iron is second in order of activity, followed by cadmium and cobalt. This suggests that the oxidase function of slightly active constant-valency ions such as cadmium can be activated. The cobalt complex showed the greatest activity in the oxidation of pyrogallol in pyridine; all the other ions are considerably inferior to it in oxidase activity. The cadmium ion is second in order of activity, but the activity of the iron ion is extremely weak.

The problem of modelling hydrolytic enzymes is much more difficult. Models of these enzymes have been obtained, from both typical chelate complexes and from some amino-acids (Table 4). Most theories of enzymic hydrolysis allow for some kind of polarisation effect[51], which may be due either to metal ions or to the action of different polar groups. The active groups of hydrolase consist of a combination of structural elements of the polypeptide chains. The active group of chymotrypsin, trypsin, and other proteases and esterases contains a definite combination of amino-acids, with histidine playing the greatest part. The mechanism of action appears to be based on acylation of the enzyme and hydrolysis of the acylated form; apart from histidine, the sequence Gly–Asp–Ser–Gly is important. Several workers[54,55] have shown that trypsin and chymotrypsin hydrolyse nitrophenyl acetate.

Free imidazole and its derivatives also have this property. The intermediate product is *N*-acetylimidazole. However, the activity of the imidazole "model" is lower than that of the enzyme chymotrypsin by a factor of 10^5. The catalytic activity of L-histidine in this reaction has also been examined; it has been found that blocking of the amino- and carboxyl groups increases the activity 3–4 times[54]. Histidine peptides have also shown hydrolytic activity. Bruice and Schmir[53] studied the catalytic properties of imidazole in the hydrolysis of phenyl acetate. These workers had in mind the part that the histidine imidazolyl groups play as components of the active sections of hydrolytic enzymes. They examined the mechanism of hydrolysis in the presence of imidazole and concluded that the most likely mechanism was one in which the imidazole reacts directly with phenyl acetate, forming phenol and some product that subsequently reacts with water to give acetic acid

and the regenerated catalyst. The product is probably an acylo-imidazole complex stabilised by the superposition of several structures:



Metal ions undoubtedly play an important part in natural hydrolytic systems. The necessity of the presence of magnesium for the hydrolysis of ATP has been interpreted by Szent-Györgyi[56] on the basis that magnesium has a polarising action on the twisted ATP molecule. It is to be expected that complex ions would produce hydrolytic effects. Wagner-Jauregg and coworkers[57] showed that some copper chelate complexes catalyse the hydrolysis of diisopropyl phosphorofluoridate (DFP). The complexes containing ethylenediamine, $\alpha\alpha$-dipyridyl, histidine, *o*-phenanthroline, and imidazole as ligands are the most active. The active complexes are unsaturated coordination compounds. In aqueous solutions the sites in the coordination sphere that form the reactive space of the complex (positions 5 and 6) are occupied by hydroxy-groups or by water molecules. Further studies showed the same regular features that the author observed in the catalase-active complexes. In particular, increased stability reduced the catalytic activity; the activity is a function of pH and depends largely on the presence of a chelate ring.

Investigation of the complexes formed by di- and tri-amines has shown that ligands of this type may be arranged in decreasing order of activity of the complexes: tetramethylethylenediamine, dipyridyl, ethylenediamine, hydroxyethylethylenediamine, dihydroxyethylethylenediamine, diethylenetriamine. It is suggested[58] that hydrolysis occurs as a result of the simultaneous action on the substrate of OH^- ions and diaquo-metal chelate ions. A complex with the substrate may first be formed, and is then attacked by OH^-. This model is of interest because the substrate (DFP) appears to play the part of "organiser", bringing the OH^- ion and the catalyst proper, copper chelate, into a suitable conformation. In enzymology it has often been noted that the substrate can have an organising influence on the components of the active centre. Anfinsen[56] has pointed out the part that the tertiary structure of proteins of hydrolytic enzymes plays in the mechanism of their action and in the level of their activity[59]. The active centre is said to be stabilised by a complex system of interactions, as a result of which secondary and tertiary structures arise; complete information necessary for the formation of these structures is contained in a definite amino-acid sequence in the extended polypeptide chain.

Anfinsen's reasoning refers to ribonuclease. Whether this picture is a general one is still undecided, but there are grounds for assuming that the active centres of enzymes could be formed at "a higher level", that is, when the course of evolution had already led to significant development of higher-order structures. It is extremely important that this fact was discovered in the investigation of protein-splitting enzymes. The gradual development of polypeptide systems led to the formation of the active centre, built up from different fragments of the twisted polypeptide chain or chains, and the emergence of this centre initiated hydrolysis processes that probably limited chain growth.

The modelling of dehydrogenases presents no formal difficulties, since a large number of reversibly oxidisable dyes are known to function by the same mechanism as the enzyme systems. The dye abstracts hydrogen from some substrate, is converted to the hydrogenated form, and then gives off its hydrogen to oxygen or another acceptor. Thus, Methylene Blue acts as a catalyst in the oxidation of many organic compounds, in particular ascorbic acid; this reaction is accelerated by light[60,61].

It is interesting to find to what extent a particular model of this type is specific for the substrate. In nature the active groups of dehydrogenase coenzymes, NAD and NADP, interact with the substrate and the corresponding protein to form dehydrogenase systems with specific activity. Therefore, before dehydrogenase models are examined, it is useful to consider the more general problem of modelling enzyme systems containing a high-molecular-weight carrier (Table 5).

The sharp increase in catalase activity produced when iron ions are adsorbed on charcoal may serve as a simple example. The porphyrin complex haemin and iron phthalocyanine are also activated by this carrier. As the activity of charcoal itself is low, the deviation from additivity is very marked. The specific effect is emphasised by the failure of charcoal to activate most other ions; also, many carriers (stannic oxide, barium sulphate, and alumina gel) inhibit the catalase activity of the ions. "Charcoal models" are obtained not only by adsorption of ions from solution, but also by charring materials containing metal compounds. It would be fairly difficult to determine the active centre in such catalysts or even to evaluate approximately the "ballast" that plays the part of an activator. Warburg[12] found that charcoals prepared by charring haematin had considerable catalytic activity in oxidation reactions. In 1932 the author found[66] that blood charcoal had a strong catalytic action on the halogenation of organic compounds; dihalogeno-substituted products were obtained from benzene, and ethyl bromide from ethanol.

TABLE 5. Models containing a high-molecular-weight component.

Active group	High-molecular-weight component	Reaction	Literature references
Haemin	charcoal	decomp. of H_2O_2, oxidation of oxalic acid	12, 21
Phthalocyanines of heavy metals	charcoal	various oxidation reactions	36
$>CH-N(C_2H_5)_2$	cellulose	decomp. of bromocamphoric acid, formation of mandelonitrile	18
Methylene Blue, thionine	starch	oxidation of metol and pyrogallol	60
Copper–histidine	insulin	oxidation of ascorbic acid	43
Copper–amino - alcohols	albumin, legumin, casein	oxidation of pyrogallol	62
Polychelate metal complexes		decomposition	63, 64
Indigo carmine	cellulose	oxidation of hydrogen sulphide	65

To examine the form of iron in charcoal of the type obtained from blood, the author studied charcoal prepared by charring haematin. Magnetic and X-ray studies indicate that the iron in this charcoal is in the form of a nitrogen-containing complex, in which the iron is probably bivalent and bonded with no more than three or four atoms of nitrogen and carbon; there is very little activating ballast present. The author observed similar effects in the adsorption of iron ions on charcoal obtained by charring sulphanilic acid. This charcoal has a very large surface area (700 $m^2 g^{-1}$) and X-ray examination shows it to be amorphous.

The nature of the bond between the active group and the carrier is clearer in the "faser-catalysts" of Bredig and Gerstner[18]. These workers prepared diethylaminocellulose by the method of Karrer and Wehrle and found that it accelerates the elimination of carbon dioxide from bromocamphoric acid. The catalyst shows optical selectivity: in the synthesis of mandelonitrile it increased the laevo--rotation. The active group of this catalyst appears to have the structure of a diamino-derivative:

$$\rangle CH{-}NH\,(C_2H_5)_2\,.$$

Krause and coworkers[67] have carried out extensive investigations of the catalytic activity of mixed hydroxides. The activating action of copper hydroxide on the catalytic function of a mixture of the hydroxides of manganese and cobalt led these workers to conclude that copper hydroxide is an analogue of the active group of the enzyme. Catalytic systems of this type are very interesting in themselves, especially as hydroxides also catalyse ester hydrolysis, that is, they behave as esterase models[68]. However, they appear to have played an important part only in the first stages of biochemical evolution, having been later replaced by other systems.

The copper ion attached to insulin, and also the copper–histidine complex bound to this protein, are models of ascorbate oxidase, according to the author's results. Nikolaev and Korpusova[62] found that the proteins albumin, casein, and legumin considerably enhanced the polyphenol oxidase activity of copper complexes with amino-alcohols and other ligands. In all these cases, fixation on carriers had only a slight effect on the visible and ultraviolet spectra. The activation of amino-alcohols on proteins appears to be due to complex formation with the amino-groups of the protein, since it is reduced when the protein is treated with formaldehyde.

Considerable activation is observed when the bond between the active group and the carrier is very weak, in contrast to the bond in the examples given above. Dyes that can change reversibly into leuco-forms have undoubted features of similarity with the active groups of dehydrogenases and with those compounds that act as intermediate links in hydrogen transfer in biological systems.

The catalytic action of Methylene Blue and thionine on the oxidation of pyrogallol and metol with oxygen, and the activation of these compounds by their adsorption on starch have been studied by Yushina[61]. The bond between the dye and the starch appears to be affected by means of the negative charges on the colloidal starch particles and the dye cations. The carrier only shows activation when it is in the colloidal state. The loss of activity produced by adsorption on starch powder thus appears to be analogous to the deactivation of the enxyme that occurs in denaturation.

The author had also shown[65] that cellulose is a good activator of the dehydrogenase function of indigo carmine. This dye can change reversibly into the leuco-form, which is rapidly oxidised by atmospheric oxygen. In the presence of cellulose the reaction is greatly accelerated if hydrogen sulphide is used as the hydrogen donor. The reaction proceeds very readily when the hydrogen sulphide solution contains trace amounts of copper and iron ions. Thus indigo carmine adsorbed on cellulose is a model for the dehydrogenase catalytic system. It is known that many enzymes of this class are activated by traces of metals.

There are interesting possibilities in the investigation of the catalytic properties of chelate polymers containing metal ions separated by organic groups. Catalysts of this type were studied by Boreskov, Keier, Rubtsova, and Rukhadze[63,64], who found that the catalytic activity of polychelates depends mainly on both the nature of the metal ion and on the nature of the organic units. Obviously, variation of the structure of the organic units opens new possibilities in controlling the steric and energetic factors in the catalytic process.

The reaction between indigo carmine and hydrogen peroxide studied by Kitsenko shows that orientation effects may sometimes be important. The degradative oxidation of the dye accompanied by bleaching is accelerated by phase boundaries of a different nature[69]. Thus the rate of the reaction increases at the aqueous solution–benzene or aqueous solution–toluene boundary and also at the solution–air boundary, etc. Here a special chemisorption effect, or the formation of intermediate products, is unlikely, but there is no doubt about the kinetic effect. From this it follows that, in general, the appearance of a new phase in complicated organic systems often involves a large number of types of possible catalytic action, even when the intermediate active products cannot be characterised.

IV. COMPARISON OF THE PROPERTIES OF MODELS AND BIOCATALYSTS

It is obvious that the more rigid the requirements that models have to meet the smaller will be their number. When the conditions that the model and the enzyme should be similar in structure and operate by similar mechanisms were added to the requirement of high activity, the number of models diminished. However, even these limitations leave too large a number of models to be considered, and they do not remove the difficulties encountered in formulating selection principles. For this reason, attention must be directed to those facets of biocatalysis which, firstly, have no analogies in ordinary catalysis, and secondly, have not been modelled in any clear form. The following features of the catalytic action of biocatalytic systems apparently differentiate enzymic from ordinary catalysis.

1. Active centres in a number of reactions are obtained as a result of the development of higher-order structures — tertiary, and probably also quaternary protein structures (hydrolase). The active centre includes not only the group of atoms directly entering into the catalytic act, but also part of the protein molecule extending far beyond its limits. This zone ensures a suitable arrangement of substrate molecules and is related to the specific activity.

2. The substrate sometimes undergoes preliminary activation. Thus, sugars are first phosphorylated before they enter the cycle of conversions that leads to pyruvic acid; amino-acids are also phosphorylated in the synthesis of the polypeptide chain, and fatty acids combine with CoA.

3. The active centre often comprises a group of atoms weakly bound to the protein and displaceable from one protein to another. The protein–substrate complex and the active group nevertheless act together, the bond between them sometimes being due to the inclusion of a metal "coupling". The specific adsorption of the substrate on the protein is one facet of the catalytic system, and the action of cofactors proper is another. Entropy and energy factors are therefore partly "disconnected". A system that might serve as a model is one in which the substrate is prepared for reaction by adsorption on a carrier to obtain the necessary orientation of parts of the molecule (or of several molecules), and in which an active centre or active species effects the catalytic reaction itself in the system.

4. The catalysts are combined in a system by principles of energy or substrate coupling; the energy of one reaction is used to overcome the activation barriers of another, and the substrate of one process is the end product of another. This needs a special organisation of a high degree of complexity (mitochondria).

5. The synthesis of the catalysts themselves is inseparable from their functions; the two processes are related by a feed-back mechanism. It has been shown that an increase in the concentration of the products of the action of certain enzymes leads to suppression of the synthesis of the enzymes themselves. The structures characteristic of biocatalysis, of course, meet these requirements. The polymer chains of peptides, including active amino-acids (histidine, for example, in hydrolysis reactions), possess very wide possibilities for the formation of active centres and the creation of higher-order structures precisely adjusted to the substrate. The substrate is activated by combining with phosphoric acid residues, while phosphoric acid (energy-rich system of pyrophosphate bonds) also enters into the composition of the active groups of the catalysts themselves (ATP, NAD, etc.).

Fixation on the high-molecular-weight carrier groups, supplemented by the action of the catalyst proper at its extreme activity, when virtually the whole substrate molecule is bound to the carrier and subjected to change at many points, means that the structure of the carrier determines the arrangement of the product. This "matrix" principle, which is very characteristic of biocatalysis, requires precise structural matching of all the participants in the reaction and leads to the phenomenon known as self-reproduction†. It is not difficult to show from an examination of its properties that a particular model is deficient in some respects, and from this it may be concluded that the make-up of biocatalysts in cells is in some way "unique". It cannot be said that these catalysts have a special type of bond or mechanism of action. There is nothing fundamentally new in the types of bonds in biological systems; they include covalent, donor–acceptor, and hydrogen bonds, as well as interactions based on steric effects (for example, clathrate), polarisation effects, etc.

The mechanism of action is, as a rule, associated with the formation of intermediate lubile forms with steric characteristics close to those of the transition complex. With model compounds, the intermediate products are usually less stable and more difficult to identify than with enzymes, but there is no reason to suppose that the fundamental reaction steps in biocatalysis differ from the corresponding stages in catalysis by less complicated catalysts.

Peculiarities become manifest at a higher level; indeed, when a number of similar catalysts are being tested, the possibility of transition to a higher level of organisation is a selection factor.

Simple systems containing catalysts arose in large numbers at the early stages of chemical evolution. Most of these quickly ceased to exist, not having the means to increase their stability. For these, evolution to a more stable state corresponded to the normal thermodynamic evolution of open or closed systems. Those that acquired the means of maintaining the level of organisation by means of feedback mechanisms with the medium obtained new means of stabilisation, and what is particularly important, new stability conditions. These conditions are not associated with extremal entropy values, or extremal values of the derivative of the entropy with respect to time; they are determined by work done by control apparatus linking external stimuli with deviations from the parameters of the system.

Let us follow the course of increasing complexity of systems from the most elementary, such as a rarefied gas, to a highly organised system, such as man. We find that the conditions corresponding to stability of the system differ substantially at the ends of this sequence. For the gas, thermodynamics precisely indicate the exact functions and conditions that determine equilibrium, but for man, or even for a less complicated living organism, adherence to the formulations of thermodynamics would lead to destruction of the system, not to stabilisation. Stabilisation is achieved by entirely different means, the development of which cannot be predicted by thermodynamics. An organism consists of mechanism, at the basis of which are molecules in a state of interaction with one another. Consequently, the gradual increase in complexity of the systems will lead in certain cases to a state in which the new systems arising are stabilised by laws different from those that controlled the transition to the more stable state in the initial systems — the precursor systems.

In fact, transition to the equilibrium state, corresponding to maximum entropy in the isolated system, or the achievement of a steady state in "flow", differs from stabilisation due to feedback systems, although these feedback mechanisms developed in the same "material" that is stabilised by the simple method mentioned above. It therefore follows that only those elementary systems could become the starting points in evolution that satisfied the fundamental requirement that stability conditions for combinations of systems should differ from those for the initial systems. It is this principle which leads to the independence from the material which has been discussed at the beginning of this review. From this point of view, we may attempt to interpret certain special features of biological evolution. Actually, as organic compounds gradually increased in complexity, new stability factors arose when catalysts were formed. Few cases are to be found in biology in which chemical control and chemical feedback occur without the participation of a catalyst. On the other hand, every simple case of catalytic action, reversibly inhibited by reaction products, is an example of chemical control. It is quite reasonable that all subsequent development should have been based on the synthesis of diverse catalysts and the perfection of mechanisms for their coordinated action.

† Interesting information on the imprints that the substrate produces on the catalyst surface may be found in a paper by Balandin [70].

Thus the process that had become the basis for the formation of living structures involved most readily compounds that were converted to elements of catalytic system and were therefore withdrawn from the sphere of operation of stabilisation laws characteristic of the simplest aggregates of heterogeneous molecules. It is characteristic of feedback stabilisation mechanisms that they prevent the system reaching a state of thermodynamic equilibrium; this gives them an advantage over all other stabilisation mechanisms. The interrelationships of a system of this "higher" order with the medium are determined by the fact that both the medium and the system will each tend to its own stable state. For the medium this will be, for example, the state of maximum entropy, and for the system, the state in which the control apparatus is stable in operation, corresponding to the minimum change in the parameters of the system for given external random influences. In this way, the characteristic equilibrium of systems of different degrees is established, the increase in entropy of the medium being related, at least phenomenologically, to the decrease in this function for the system.

Further increase in the complexity of the controlling apparatus and the general growth in the degree of organisation of the system is only possible if the associations arising will increase the stability of all less complex apparatus, in the same way as the conscious intellectual activity of man is directed towards the stabilisation of all the mechanisms on which his existence depends in some way or another.

Evolutionary selection by the application of an immense number of tests to the enormous number of biocatalyst "models" has limited adoption to those that were found suitable for the synthesis of catalyst systems with feedback, capable of sustaining the course of evolution to systems of higher degree with still more diverse stabilisation possibilities. The modelling of chemical self-stabilising systems is one of the most interesting problems of the future science of catalysis.

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ANODIC OXIDE FILMS

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I. INTRODUCTION

Oxide films on metals are widely used in the national economy, in various electrochemical devices, in condensers, in rectifiers, in chemical sources of current, and also for protecting metals against corrosion.

The metal–oxide–electrolyte system exhibits an appreciable capacity and can rectify alternating current over a wide range of potentials. Therefore such a system finds a wide use in electrical devices.

Oxide films also have independent importance in studying electrochemical reactions on metals, since under specific conditions it is necessary to take into account that all metals are covered with oxide films.

There is now considerable material on the experimental and theoretical problems of anodic oxide films, which it is difficult to generalise in a single review. Hence the present article will consider only certain questions concerning mechanism in the formation of anodic oxide films and of their properties.

This review considers the kinetic mechanisms of the growth of oxide films during anodic oxidation and also certain properties of films on valve metals.

II. GROWTH OF ANODIC FILMS

Anodic oxide films on metals or semiconductors are formed in a solution of electrolyte on applying a potential more positive than the equilibrium potential. Afterwards as the metal becomes covered by a thin continuous layer of oxide, which is insoluble in the electrolyte, an electrostatic field is established in the oxide. This field causes ions of metal or oxygen to move through the oxide layer, which also leads to growth of the film. For the formation of each new layer of oxide an additional potential dv is required, which is added to the existing potential in the film.

It is found experimentally that the quantity dv/dx does not vary as the thickness increases, but for certain metals there is a departure in one direction or the other.

The growth of the film is greatly hindered by processes at the boundaries of the film with the metal and with the electrolyte[1-4].

The formation of centres of crystallisation and also the thickening of the films requires overpotentials of from 10 to 1000 mV. These are made up of; (1) the energy for the removal of a metal ion from the lattice to the metal–oxide boundary; (2) the kinetic energy of the metal ion through the film; (3) the energy for the exchange of charged particles between the electrode and the solution at the oxide–electrolyte boundary.

In their structure oxide films can be divided into porous and continuous (pore-free). The resistance of porous films is of the order of a few ohms, and their potentials at the time of growth are near to equilibrium, they are almost invariably crystalline, and their growth is essentially by diffusion of the ions through the oxides or through the electrolyte. Such films are formed on cadmium, zinc, and magnesium.

Vermilyea[5] considers that continuous films are formed during simultaneous oxidation of metal at all points of the surface.

Misch[6] thinks that the nature of the oxide film depends on the value of the ionic potential (the ionic charge divided by the radius), the lattice type of the metal and oxide, and also the bond energy. The adhesion of the oxide particles depends on the ionic nature of the oxide, the resistance to impregnation by water, and the extent to which the ratio of the molar volume of the oxide to the molar volume of the metal (the Pilling and Bedworth ratio) exceeds unity. Continuous growth of the film depends on the overall ionic current in the film, in which connection the following facts must be considered: (1) the overall electrical conductivity of the oxide, and (2) the transport numbers of the ions, electrons, and holes.

If the oxide is an electronic semiconductor, then all the current is used in the discharge and liberation of gaseous oxygen, the ionic current will be insignificant, and the thickness of the film will not increase — such a reaction takes place on titanium[7].

Another type of reaction is the processes taking place on tantalum[8], aluminium[9], zirconium, for which the effectiveness of the anodising of the pure metal is 100%. The

growth of such films begins with a monolayer and continues uniformly over the entire thickness approximately up to 10^{-4} cm; during this period the resistance of the film can reach a million ohms.

Such films can be crystalline, vitreous, or amorphous. They exhibit unipolar conductivity[10].

On certain metals, *e.g.*, aluminium, laminar oxide films are formed[11-16]: the layer close to the metal is continuous and that which is near to the solution is porous. As the thickness increases, conditions for the appearance of cracks are aggravated[17-21]: overheating in defect positions owing to the passage of a steady current through the film, transformation of the oxide from one modification to another, etc.

III. NON-POROUS FILMS: EMPIRICAL RELATIONSHIP BETWEEN IONIC CURRENT, FIELD, AND TEMPERATURE

Fig. 1 gives the i *vs.* V relationship for valve metals coated with an oxide film, and shows that for a negative potential the current increases rapidly, the electrode process during this being accompanied by the liberation of hydrogen. In anodic polarisation the current is vanishingly small and rather irreproducible right up to that potential at which the ionic current exceeds the leakage current, which then rapidly increases with the potential. The passage of an anodic current is accompanied by the liberation of oxygen. This is linked with electronic conduction by the film.

The theoretical ionic current occurs at all potentials above the reversible oxygen electrode potential, and in practice it is insignificant in comparison with the leakage current in small fields.

As soon as the field potential is made sufficiently high for the appearance of an ionic current, the passage of the latter through the electrode causes growth of the film. This growth can be brought about in either potentiostatic or galvanostatic conditions.

When a direct current is passed through the film the formation of each new layer requires a field of potential dv additional to that already existing in the film. The quantity dv/dx is termed the differential field potential.

The relation between the growth rate of the potential and current density in such a case can be linked with the growth rate of the film, which is:

$$\frac{dD}{dt} = \frac{iM}{ZF\rho},$$

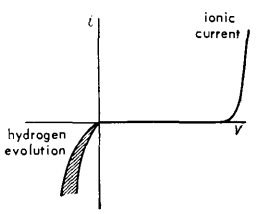

Fig. 1. Voltampere characteristics of an oxidised tantalum electrode.

where i is the ionic current density, F Faraday's number, M the molecular weight of the oxide, ρ the density of the oxide, D the oxide thickness, and t the time.

If the differential field potential E_d is constant, then the rate of increase of the potential is:

$$\frac{dv}{dt} = E_d \frac{dD}{dt} = iE_d \frac{M}{ZF\rho}. \quad (1)$$

For tantalum at room temperature, $dv/dt = 3$ V s^{-1} for $i = 10^{-3}$ A cm^{-2},[22] the field potential necessary for an ionic current of 10^{-8}–10^{-1} A cm^{-2} to flow in the film being 10^6–10^7 V cm^{-1}, or 0.01–0.1 V $Å^{-1}$. It is quite obvious that under such high electric field potentials Ohm's law is not obeyed.

The equation for the ionic current and electric field in arbitrary systems is in general well described by the relation:

$$i = 2A \operatorname{sh} BE. \quad (2)$$

For high potential gradients, Eqn. (2) transforms into the equation first given by Günther-Schulze and Betz[23]

$$i = A \exp BE, \quad (3)$$

where A and B are constants which depend linearly on temperature. Eqn. (3) satisfactorily describes the relation between i and E to a first approximation.

At low electric fields Eqn. (2) has the form:

$$i = 2ABE. \quad (4)$$

It is evident from Eqn. (3) that the slope $dE/d(\ln i)$, analogous to the Tafel slope, has a linear dependence on temperature. However, the experimental results show that, in certain cases, the temperature dependence is non-linear.

The equations mentioned do not reflect completely the film growth process, since they do not take into account phenomena at the metal–oxide and oxide–electrolyte boundaries.

To express more fully all the phenomena brought about by the field in the oxide film, it is convenient to introduce the concept of overpotential in the formation of oxide, which by analogy with the overpotential in hydrogen liberation, is determined in any electrode process as the difference between the potential drop at the oxide–solution boundary and the potential drop which there would be at the electrode if it were reversible for the given electrode reaction, or as the potential of the oxide electrode in relation to a reversible auxiliary electrode.

The connection between the oxide formation overpotential η and the applied potential, *i.e.* the electric field potential E in the body of oxide and at the metal–oxide and oxide–electrolyte boundaries can be represented as follows. Assuming that in the hypothetical reversible state the potential drops at the metal–oxide boundary, in the body of the oxide, and at the oxide–electrolyte boundary are respectively Φ_1^e, Φ_2^e, and Φ_3^e; then the overpotential for oxide formation is expressed as the sum of the potential drops at the metal–oxide boundary $(\Phi_1 - \Phi_1^e)$, in the body of the oxide $(\Phi_2 - \Phi_2^e)$, and at the oxide–electrolyte boundary $(\Phi_3 - \Phi_3^e)$:

$$\eta = (\Phi_1 - \Phi_1^e) + (\Phi_2 - \Phi_2^e) + (\Phi_3 - \Phi_3^e), \quad (5)$$

where Φ_1, Φ_2, and Φ_3 are the respective potential differences under the applied electric field.

As the quantities $(\Phi_1-\Phi_1^e)$ and $(\Phi_3-\Phi_3^e)$ are independent of the oxide thickness and depend only on the polarising current, the overpotential of the film growth process will be

$$\eta = \Phi_2 - \Phi_2^e \qquad (6)$$

and

$$E = \frac{\eta}{D},$$

applying the condition that, in the hypothetically reversible state, the field in the film is vanishingly small in comparison with that which brings about film growth.

IV. THEORY OF THE GROWTH OF ANODIC FILMS

Contemporary theories of the growth of anodic oxide films are based on the celebrated theory of Mott and Cabrera[24] and Verwey[25], developed for the oxidation of metals in the gas phase.

Electrons can, with a certain probability, penetrate from the depth of the metal through the thin oxide film (10 Å) to the surface and ionise adsorbed oxygen atoms. This produces an electrical double layer with a certain potential difference, which at the film thickness mentioned gives a potential gradient of 10^7 V cm^{-1}. The presence of such a field permits cations to diffuse throughout the film.

According to Mott and Cabrera, the volume charge is small in sufficiently thin films, therefore there are no appreciable changes in the field in the body of the film (the field is considered to be homogeneous in the film), and hence the ionic field current is determined by the energy for the escape of a metal ion at the metal–oxide boundary according to the equation:

$$i = n'\nu' \exp - \{(w' - q'a'E')/KT\}, \qquad (7)$$

where ν' = vibration frequency of the ion in the metal lattice, w' = activation energy for the escape of an ion from the metal lattice, q' = ionic charge, a' = distance from maximum to minimum potential energy, E' = field potential, n' = surface concentration of the metal ions, K = Boltzman's constant, T = absolute temperature, and i = ionic current density.

Mott assumed that the concentration of carriers in the body of the film was not constant but changed under the influence of the field until the current in the mass of the film:

$$i = 2a\nu n \exp\{(w - qaE)/KT\} \qquad (8)$$

became equal to the current through the oxide metal boundary, *cf.* Eqn. (7). At this point, the concentration of ions n inside the oxide became equal to the surface concentration of metal ions. The slope $dE/d(\ln i) = kT/qa$ must be proportional to the temperature.

Verwey's theory, in contradiction to that of Mott, assumes that the ionic current in the film is determined by the movement of the ion through the bulk of the film, and the dependence of the ionic current on the electrical field is expressed by an analogous equation.

The use of the anodic method of oxidising metals – under more accurately defined conditions, permitted a more thorough investigation of the oxide film growth process.

Experimental results from studying the temperature dependence of anodic oxidation and a study of the transient processes showed that Eqn. (7) describes only the motion of individual ions in the film under conditions of an electric field of high potential and that the behaviour of the total ionic current in the film is more complex. It was found that the values of a and w in the kinetic equation for current are considerably greater than predicted by theory (*cf.* the Table). These two theories can be considered as boundary cases of a single theory.

Young[26] has given the fundamental electric field equation embracing these two cases as limits:

$$E(x) = E_0 + \frac{1}{\beta}\ln\{[n_0(n_0 - n)\exp(-\beta 4\pi q x n/\varepsilon)]n\}. \qquad (9)$$

Here n = concentration of mobile ions in electrically neutral oxide, n_0 = concentration of mobile ions in the given field, ϵ = dielectric constant, E = field potential in oxide, x = = coordinate, q = ionic charge, a = distance from maximum to minimum potential energy, and $\beta = aq/KT$.

The quantities E_0 and n_0 in Eqn. (9) are the values of E and n at $x = 0$. In this case when x is large, *i. e.* in thick films:

$$E(x) = E_0 + \frac{1}{\beta}\ln\frac{n_0}{n}. \qquad (10)$$

Substituting in this equation the values of E and n derived under the assumption that the rate of motion of an ion through the metal–oxide boundary is equal to rate of motion of an ion in the body of the film, we obtain the Verwey equation for ionic current:

$$E = \frac{1}{\beta}\left\{(\ln i/2a\nu p) + \frac{w}{KT}\right\}. \qquad (11)$$

From Eqn. (1) we see that the electrical field is determined by the bulk properties of the film. It can be shown that when x is small Eqn. (9) transforms into Eqn. (7).

By determining the temperature dependence of the rate of growth of an anodic oxide film, Vermilyea found that between 0° and 80° the Tafel slope is independent of temperature.

Young[27] also confirmed this between 20° and 60° for films on niobium. The relation

$$\frac{dE}{d\ln i} = \frac{KT}{qa}$$

is valid between these temperature limits.

The experiments of Scholte and van Geel[28] and of Young[27,29] showed that the application of an electric field on an Nb_2O_5 film causes an increase in the concentration of mobile ions, and the space charge in the film attains an appreciable value, which depends on the current density. After switching off the forming potential a pseudo-equilibrium state is slowly established in the film – the distributed volume charge.

TABLE. a and w for ionic conductivity in a high field.

Metal	Activation energy, w, eV	a, *cf.* Eqn. (7), 10^{-8} cm	Reference
Ta	1.39	2.5	27
Al	1.55	2.5	48
Zr	1.34—1.84	2.3—3.7	1
Zr	1.04—1.19	2.8—4.4	83
Nb	0.71—0.76	3—4	33,84
Nb	1.19	2.4	85

By measuring the impedance of an oxidised niobium electrode immediately after breaking the external circuit, Young obtained curves for the increase of capacity with time for various space charges. The rise in capacity on the curves depended on the temperature but not on the ionic current density.

On the basis of these measurements and also of measurements of the impedance of a niobium pentoxide electrode as a function of frequency Young concluded that the resistance of the oxide changes exponentially with distance from the metal–oxide boundary to the oxide–electrolyte boundary, *i. e.* the field changes the concentration of mobile ions.

The percentage ratio of the change in reciprocal capacity for a given change in the logarithm of the frequency becomes independent of thickness. Hence the resistance of the layers of the film at the boundary with the metal and at the boundary with the solution must be considered independent of thickness (its total thickness), *i. e.* the degree of departure from stoichiometry under these conditions will be determined by the equilibrium at the metal–oxide and oxide–electrolyte boundaries.

The role of the space charge in the kinetics of the growth of the anodic film and the quantitative interpretation of the space charge were first given by Dewald[30,31] on the basis of a model of the oxide film developed by Haring[31] (*cf.* Fig. 2).

Fig. 2 shows that during escape from the metal to a distance b, a mobile ion must overcome a higher potential than during its further motion into the film, where the potential barrier equals u.

By considering the film as a lattice of stoichiometric composition through which metal ions move under the influence of the electric field, and taking into account the space charge, Dewald showed that the behaviour of such a system depends on a critical factor δ (a non-dimensional quantity), which is determined both by the lattice parameters of the oxide and by the experimental conditions:

$$\delta = \beta\gamma n_0 D = \left[\frac{4\pi q^2 (m_s \nu_s)^{a/b}}{K\nu}\right] \{\exp[(u - \varphi a/b)/KT]\} \frac{D}{T} i^{(1-a/b)}. \quad (12)$$

Here u = activation energy for the motion of an ion between two position of equilibrium in the absence of an electric field, $2a$ = distance between the two equilibrium positions, ν = vibration frequency of an ion in an interstitial position, ν_S = vibration frequency of a metal atom at the surface, n_0 = concentration of the ions at $x = 0$, φ = activation energy for the diffusion of an ion from the lattice into the film, m_S = surface density of the metal ions, and D = film thickness.

When δ is small, corresponding to a small space charge, the film growth kinetics are determined by phenomena at the metal–oxide boundary. When δ is large, ~10 at a film thickness of 1000 Å, the rate of formation of the oxide is almost completely determined by the bulk of the film. Under a high electric field electrons are removed from the film and the interstitial motion of the ions is not electrically compensated, as a result which a space charge is set up.

For the mean electric field potentials Dewald obtained the equation:

$$\bar{E} = E_0 + \frac{1}{\beta}\left\{\left(1 + \frac{1}{\delta}\right)\ln(1-\delta) - 1\right\}, \quad (13)$$

from which it is evident, that at any point of the film the field is determined by two quantities: the surface charge E_0, due to the motion of the ions, and a quantity related to the space charge.

Eqn. (13) gives quite a simple relationship for $\delta \gg 1$ and $\delta \ll 1$, but is rather complex when δ is close to unity.

The interpretation of parameter δ also permitted the suggestion that the Tafel slope at certain current densities, oxide film thicknesses, and ratios of parameters a/a' and w/w', can be independent of temperature. The theory was confirmed by the experiments of Vermilyea[21] and Young[33].

Dewald's theory was an advance towards determining the combination of complex processes taking place during the anodic oxidation of metals and their interrelation.

The phenomena observable during the film growth process which are not covered by Dewald's theory include transient processes. The so-called transient processes reflect the non-steady behaviour of the film between two stationary conditions corresponding to two different values of the field potential. The transient processes were investigated suddenly changing the electric field in the film[34], which brings about two successive processes — an initial instantaneous, and then a slow, change in current.

When the current was increased instantaneously[35,36] the initial rise in potential shifted to a lower stationary potential corresponding to a new current (*cf.* Fig. 3). The value of the excess field was independent of the initial current density in the range 2×10^{-6} to 4×10^{-4} A cm^{-2}, of thickness, and of temperature, and depended only on the ratio of the final and initial current densities and on the method of interrupting the current.

The second method of studying the processes taking place in the transient state consists of the application of an alternating potential of low amplitude in addition to the constant forming potential[35].

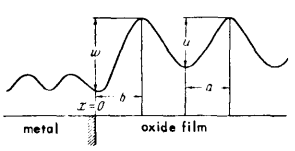

Fig. 2. Potential curve for a metal ion in a high electric field. x denotes the equilibrium position of the ion at the surface of the metal.

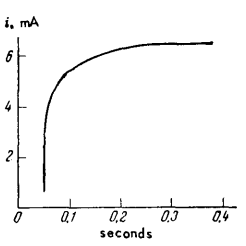

Fig. 3. Transient state of the ionic current in a Ta_2O_5 film at the moment of change of an electric field from 0.057 to 0.062 V Å^{-1} at 81°.

The activation energies and the distances between the two equilibrium positions in the transient state, calculated by the two types of experiment, were anomalously high, 0.7–1.4 eV for w and 2.4–2.8 Å for a.

Unlike Verilyea and van Geel[37], who explained the anomalously high values of a and w by relaxation phenomena in the structure of the film, Young and Dewald consider the existence of the transient states in a film during a sudden change in applied potential to be the result of a change in the concentration of mobile carriers in the film.

These experimental results on transient processes show that in a sufficiently high field the rate of transfer of the ions through the film is determined not only by the applied potential but also by the carrier concentration gradient, and therefore cannot be described by any of the equations proposed earlier.

The experimental results on transient processes in the film were explained in theory proposed by Bean *et al.*[38] and simultaneously by Dewald[36], Young[26,39], and Winkel *et al.*[35]

From experimental results on ionic conductivity of oxides in high electric fields, Maurer[40] suggested a relation between the concentration of the moving ions in the oxide and the magnitude of the field. For a crystalline oxide the increase in ionic conductivity under the influence of the high-potential field is analogous to the formation of Frenkel defects. The possibility of formation of ionic conductivity in this way in electric fields with potentials of 6×10^6 V cm^{-1} was confirmed experimentally by Tompkins and Jacobs[41].

Bean *et al.*, and later Dewald, used this theory to explain experimental results on transient processes in oxide films.

The theory was based on the assumption that ions are mobile and that holes are immobile, which is improbable under the conditions of electric fields of such high intensity. The concentration of mobile ions, n, was taken to be dependent on the field, but the oxide was assumed to be neutral. The rate of formation of Frenkel defects is given by the equation:

$$(N_0 - m)\,\nu_1 \exp\{-(w_1 - qa_1E)/KT\}, \qquad (14)$$

where N_0 = concentration of metal ions in the lattice, m = = concentration of Frenkel defects, and a = one-half the distance between neighbouring positions of equilibrium of the ion. All parameters with subscript 1 relate to the escape of ions from the metallic lattice.

By assuming that the rate of recombination (capture of an ion by a hole) is $im\sigma$, a differential equation for the concentration of the holes was obtained:

$$\frac{\partial m}{\partial t} = (N_0 - m)\,\nu_1 \exp - \{(w_1 - qa_1E)/KT\} - im\sigma. \qquad (15)$$

By putting $m = n$, we obtain:

$$i = 2a_2 m\nu_2 \exp - \{(w_2 - qa_2E)/KT\}. \qquad (16)$$

Here the parameters with subscript 2 relate to interstitial movement. In the stationary state:

$$\frac{\partial m}{\partial t} = 0, \qquad (17)$$

then at $N_0 \gg m$, Eqns. (15) and (16) are transformed into:

$$m = \left(\frac{\nu N_0}{2\sigma a_2\nu_2}\right)^{1/2} \exp - \frac{w_1 - w_2}{2KT} \exp \frac{q(a_1 - a_2)}{2KT}; \qquad (18)$$

hence the rate of anodic oxidation is:

$$i = 2a_2\nu_2 \left(\frac{\nu_1 N_0}{2\sigma a_2\nu_2}\right)^{1/2} \exp - \frac{w_1 - w_2}{2KT} \exp q\frac{a_2 + a_1}{2KT}. \qquad (19)$$

Eqn. (18) agrees in external form with Mott's equation for ionic current. The only difference is in the treatment of the quantities a and w. The authors consider a to be a continuous function of the field potential. The equation for the field potential shows the effect on the rate not only of ionic motion, but also that it brings about other changes in the film and these secondary changes affect the ionic current.

Such secondary changes can be of two types. The first is that the field changes the concentration of the moving ions by creating Frenkel defects — the values of a and w then become greater.

The second change[34,42] is that there is an alteration in the local ionic configuration of the film, *i. e.* its parameters and the activation energy of the escape and interstitial motion of ions are changed. This explanation was confirmed experimentally by Verkerk *et al.*[43]

Young[44,45] studied the transient processes in the oxidation of a tantalum electrode. He observed that during a sudden increase in the potential of the field applied to an electrode with a low initial concentration of Frenkel defects, there is an increase in the ionic current, initially slow and then rapid. This contradicted the statement that † = 0, *i. e.*, that the current is maximal at $t = 0$.

Young concluded from these results that Frenkel defects arise as a result of a cascade process, which drive ions out of the lattice of the oxide into the interstices, and not as a result of the interconnected action of field and thermal diffusion in the oxide.

V. PROPERTIES OF NON-POROUS OXIDE FILMS

The properties of pore-free anodic films of the Ta_2O_5 and ZrO_2 type depend significantly on whether or not they are in contact with the electrolyte. The applied potential in the metal–oxide–metal system is a measure of the difference in chemical potentials along this system, *i. e.* in the direction of the field, and the driving force of the current is the equalisation of the Fermi levels. In the metal–oxide–electrolyte system, owing to the electrochemical reaction at the oxide–electrolyte boundary the applied potential includes the overpotential of the liberation of hydrogen in cathodic polarisation, or of oxygen in anodic, depending on the direction of the current. For this reason the voltage–current characteristics of the dry and moist systems can be compared only with the proviso that the electrochemical reaction at the oxide–electrolyte boundary is taken into account.

Young considers that in the region of near-stationary potentials one of the reactions:

$$OH^- = O^{2-} \text{ (in the oxide)} + H^+,$$

$$5OH^- + 2Ta^{5+} \text{ (in the oxide)} = Ta_2O_5 + 5H^+,$$

takes place, according to which stoichiometry breaks down in the outer layer of the oxide due to the introduction of oxygen.

† Symbol(s) missing from Russian text (Ed. of Translation).

The electrical conductivity of oxide films in anodic polarisation depends on the magnitude of the applied potential[40,46]. At small potentials the conductivity is electronic and the dependence of the current on potential obeys Ohm's law. When sufficiently high electric fields are applied the conductivity is ionic and it obeys other relationships[47,48].

1. Electronic Conductivity

The electronic component of the anodic current in so-called barrier films, *i. e.* in films with unipolar conductivity, falls with increase in the applied potential less rapidly than the ionic component[49]. This circumstance allows them to be separated and studied independently. The electronic conductivity of thin oxide films was studied by Charlesby[48,50], by Vermilyea[51], and by other investigators, who established that the dependence of electronic current on field potential is expressed by a hyperbolic sine relation. Frenkel's theory[52] was used to explain the experimental results in terms of the electronic current mechanism.

Vermilyea advanced the following mechanism for electronic conductivity: in the film there is a potential barrier of breadth $2a$ and height u through which the electrons must pass. The presence of an electric field decreases the barrier and increases the probability of the motion of the electrons in the field direction.

Vermilyea showed that, at a potential below the formation potential the electronic current which flows through the film is a function of the potential gradient in the film.

$$i = 2A\exp\left(-\frac{u}{KT}\right)\mathrm{sh}\left(\frac{eaE}{KT}\right), \qquad (20)$$

where A is a constant, i the electronic current density, and E the field.

The field changes the lattice parameters, allowing the electrons to pass through a symmetrical potential barrier of height u and breadth $2a$.

Vermilyea started from the semiconductor nature of the oxide film and considered electrical conductivity to be the result of increased electron emission in the conductivity zone under the influence of the electric field. He showed that when there was a field of 5×10^6 V cm^{-1} in the film the probability of the motion of electrons by a tunnel mechanism was 100 times greater than by thermal excitation.

The conductivity in the film

$$\sigma = A\exp\left(-\frac{\epsilon_0 - |V_0|}{2KT}\right) = \sigma\exp\left\{\left[\frac{q^3E}{\epsilon}\right]^{1/2}/KT\right\} \qquad (21)$$

on applying the field is increased owing to the Schottky effect. Here E = electric field, ϵ_0 = breadth of forbidden gap, $\epsilon_0|V_0|$ = breadth of forbidden gap on applying the field, q = charge on the electron, and ϵ = dielectric constant of the oxide. According to this equation, there is a linear relationship between $\ln i$ and $E^{1/2}$, as Charlsby showed[48].

Vermilyea calculated that 10^6 traps arise per 1 cm^3 in ZrO_2, *i. e.* a number quite small in comparison with the other semiconductors (10^{14}–10^{20}) and by this explained the low conductivity in oxides.

The electronic conductivity in an oxide film is evidently not homogeneous throughout its entire thickness.

Scholte and van Geel[28] concluded, from a.c. measurements of the resistance of an oxide film, that its resistance consists of several resistances connected in series, the resistance of each element depending on distance. According to this model, the film consists of a part with moderate resistance and another part whose resistance is appreciably greater and is a function of distance (*cf.* Fig. 4). The changes in resistance of the oxide with distance were also explained in terms of variation in the composition of the oxide with distance by other investigators[53–55].

Since the distribution of the electronic current in the film has not been studied accurately, only the lower limit of conductivity can be determined.

Vermilyea calculated that for Nb_2O_5 films of thickness 2000 Å, the total current at a potential of 100 V is 10^{-8} A cm^{-2}, hence the resistance of the oxide film should be 10^{15} Ω cm.

2. Rectification

Oxide films on niobium, bismuth, antimony, zirconium, and other valve metals have the property of unipolar conductivity[56]. They conduct electricity in one direction only. Walter[57] reported the ability of zirconium to rectify alternating current. Carmody[58] compared the coefficients of rectification by oxide films on zirconium and tantalum in dilute sulphuric acid and also studied the use of zirconium in electrolytic condensers.

Ta_2O_5 films sharply change their electrical conductivity on being immersed in electrolyte solution; the current which passes through even quite a small area (10^{-2} cm^2) can change by 10^4 times when the sign of the polarisation is changed.

Taylor and Haring[59] observed the evolution of hydrogen and deposition of copper on a tantalum electrode covered with an oxide film.

If instead of the electrolyte, a layer of metal is evaporated on to an Al_2O_3 oxide film, then the metal–oxide–metal system initially appears to be short-circuited, but on increasing the potential the circuit is broken by vaporisation of metal situated inside the pores and its penetration into the conducting side of the film. After disconnection such a system is an insulator at all potentials[60].

Although the property of the metal–oxide–electrolyte system to stop the current in the anodic direction was discovered long ago, this phenomenon has not yet been explained properly. Although the mechanism of current rectification by porous films has recently been clarified[61–63], in the

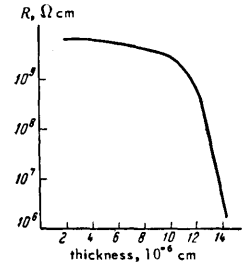

Fig. 4. Change in the resistivity of the film with its thickness.

case of continuous films there are very many experimental results which cannot be explained by any of the existing theories.

The large number of theories of the nature of unipolar conductivity of oxide films can be divided into two groups.

The first group consists of the theories based on the assumption that structural defects are present in the film — cracks which are filled with electrolyte and the latter for various reasons (concentration polarisation, Faraday rectification) exhibit conductivity only in the cathodic direction. This group includes the electroosmotic theory developed in 1930.[61] An indispensable condition of this theory is the existence of pores through the oxide film. On applying a potential to the $Al-Al_2O_3$-electrolyte system, the electrolyte in the pores of the oxide is subjected to the action of two forces: that of the electrostatic attraction of the condenser plate striving to draw electrolyte into the pores up to contact with the second plate, and that of an electroosmotic force, which can act either to assist or inhibit conduction, depending on the electrolyte and oxide combination. During anodic connection, the electroosmotic force opposes the electrostatic one and drives out the electrolyte from the pores of the film, converting it into an insulator. In the cathodic direction, these forces act in the same direction. This theory was confirmed by Zakgeim's experiments[62], which showed that the rectification coefficient of the $Al-Al_2O_3$-electrolyte system increases with the valency of the cation in the electrolyte.

The second group of theories connects unipolar conductivity with the semiconductive nature of the film. In this group two boundary tendencies can be distinguished. One consists in unipolar conductivity being determined by the existence of $p-n$ transition in the film and the oxide-electrolyte boundary takes no part in cathodic conductivity[64]. The other[65,66] considers, on the contrary, that cathodic conductivity is the consequence of electrochemical reaction at the oxide-electrolyte boundary, producing a change in the stoichiometric composition of the film and hence the emergence of conductivity.

Günther-Schulze[67] considered, in his various works, that unipolar conductivity is determined by the asymmetrical properties of the discharge through gaseous traps in the film. Subsequent experimental results obtained by him and his coworkers introduced a change in the original theory: in the cathodic direction oxygen leaves the oxide lattice, converting it into a semiconductor with an excess of metal. In this case a very high oxygen mobility is assumed. van Geel[68,69] considers that unipolar conductivity in the oxide film is determined by the presence of a $p-n$ transition.

Taylor and Haring[59] also explain their experimental results on a solid electrolytic condenser by the presence of a $p-n$ transition in the oxide.

Dekker and van Geel[70] used a bridge to compensate for the capacitative current in investigating unipolar conductivity of Al_2O_3 films. With the aid of a cathode oscillograph they thus succeeded in separating the conductivity current from the total current during the polarisation of the specimen by an alternating potential. The cathodic current on the film at the given potential was greater in that quarter-cycle where the cathodic potential is decreasing than in the quarter-cycle in which it is increasing. This gave hysteresis on the current *vs.* potential curve (*cf.* Fig. 5). These experiments did not permit unambiguous conclusions to be drawn about the reason for unipolar conductivity.

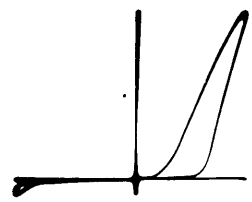

Fig.5. Voltampere characteristics of an oxide film for a sinusoidal potential at a frequency of 200 c s^{-1}.

Parallel change of the capacity and resistance in the compensating circuit in these measurements did not correspond to the equivalent circuit of the test system and, moreover, in this change the active and reactive constituents of the impedence have a complex relation to the potential.

van Geel and Bouma[71] used an improved method for similar measurements. They found that the hysteresis loop increases with time during polarisation by an alternating current and decreases with increase in frequency. The effect is considered to be the consequence of reversible change in the stoichiometric composition of the oxide.

van Geel and Pistorius [? Bouma (Ed. of Translation)][72] found that the longer the period of preliminary anodic polarisation the less the cathodic current. It was found that a sixfold increase in the thickness of the film requires the potential to be increased by only 30% in order to obtain the same current. On the basis of this it was concluded that the i *vs.* v relationship for cathodic current is a function of thickness.

van Geel and coworkers[28,67,73,74] studied the $Al-Al_2O_3$-electrolyte, $Ta-Ta_2O_5$-electrolyte, and $Zr-ZrO_2$-electrolyte systems under various conditions. It was found that at high current density the cathodic polarisation produces good conductivity in both directions but the conductivity of the oxides in the anodic direction decreases with time.

It was also shown that the production of conductivity in the cathodic direction in the oxide film depends on time and that in zirconium, for example, similar excitation requires an appreciable time. The authors assumed that rectification is determined by a $p-n$ transition at the boundary of the two layers of the film: the layer adjoining the solution (of p type) and with the remaining part of the film (n type).

Sasaki[64] considers that rectification is determined by the presence of a $p-i-n$ transition in the film.

From experiments with a mercury probe, Vermilyea[75] established that the oxide film has separate portions, area $\sim 10^{-2}$ cm^2, with conductivity a hundred times greater than the conductivity of the main surface of the oxide. A current of 10^{-9} A passes through such a place of reduced resistance in both directions up to considerable potentials. Evolution of hydrogen bubbles is observed at these places during cathodic polarisation.

Vermilyea also showed that the anodic leakage current (electronic constituent of the formation current), like the cathodic current during cathodic polarisation, increases with the film thickness at a fixed oxygen overpotential. He assumes that the conductivity of the film in the cathodic

direction can be the consequence of dislocations originally present in the metal lattice and then in the oxide – sections of low conductivity on which he observed evolution of hydrogen.

In measuring the impedance of oxidised zirconium and niobium electrodes, Young[29,46] found that at a given potential, tan θ (the tangent of the dielectric loss angle) increases with the thickness, and for a fixed thickness the leakage current increases with decrease in frequency. At the first moment of cathodic polarisation the film resistance increases, but then falls, which the author explained by penetration of H^+ at the dislocations. The leakage current fell with time at constant potential.

Young[76] obtained results on the cathodic liberation of hydrogen at the surface of oxides prepared by various methods; these results were also interpreted by the presence of cracks, mechanical defects in the film, through which hydrogen can reach the metal.

By cracks Young implies also imperfections in the structure of the oxide film[77] which bring about packing stresses in its construction, due to non-uniform oxidation of the metal. The non-uniform oxidation of the metal is facilitated by the presence of various impurities and lattice defects. Imperfections in the periodic structure of the oxide lattice can appear as cracks or in other forms.

Young assumes that cracks or, more probably, dislocations are those portions which have good conductivity in the cathodic direction and less in the anodic direction. As acceptors, protons create conductivity in the film under the condition that defects (cracks) exist in it. However, Young does not exclude the possibility that, in the absence of cracks, the film does not lose its property of unipolar conductivity.

Fig. 6 shows the frequency dependence of capacity for films of various thickness. Young explained the observed departure from a rectilinear dependence by the existence in the film of cracks, whose dimensions must increase with thickness. In cathodic polarisation, hydrogen ions, being small, penetrate these cracks and are discharged there as H_2. In this, part of the hydrogen is liberated at the surface of the oxide. However, the author does not exclude the discharge of hydrogen also being localised and in the case of distortion of the film, with its subsequent conversion into an n-type semiconductor. If the film contains.... [line omitted from Russian text (Ed. of Translation)] normal semiconductor similar to zinc oxide or germanium (*cf.*

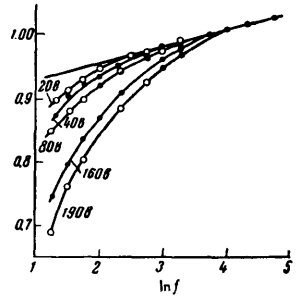

Fig. 6. Dependence of capacity on frequency for films of various thicknesses.

Dewald's work[78]). This does not persist on thin films, where the space charge region is restricted to the thickness of the film.

Young[44,45] assumes that the application of the electric field causes a change in the electronic structure of the film. This change is characterised by two successive processes: (1) disruption of the cathodic resistance is very rapid due to the delay of the conductivity in the cracks, and (2) changes in the stochiometry which change the film into a conductor.

He considers that for the anodic direction the film should be considered free from space charge and carriers. The field at the oxide–electrolyte boundary necessary for the injection of electrons from the solution into the film must be continuous through the whole film, since the overpotential of oxygen at the oxide–electrolyte boundary is distributed between two layers: in the outer layer of the oxide film and in the double layer at the oxide–electrolyte boundary.

Schmidt[65] investigated the behaviour of an oxidised tantalum electrode and n-type silicon in anhydrous solutions of NH_4NO_3 in liquid ammonia and of RuI_2 in liquid SO_2. In the first solution, which contained protons, rectification took place, but in the second where protons are absent there was no rectification. This suggested that during the period of cathodic polarisation protons enter the oxide and during the period of anodic polarisation they leave it. The protons in the oxide create donor centres which determine the conductivity of the oxide.

Investigation of cathodic currents on oxidised electrodes[66,79] showed that the magnitude of the cathodic current for a given potential depends on the size of the cation in the electrolyte. Evidently the electric field of the ion creates a potential barrier at the oxide–electrolyte barrier.

Smith[80,81] concluded, from a study of the i *vs.* v relation for oxide electrodes, that the oxide film is an insulator at whose boundary with the electrolyte there is injection of carriers during both cathodic and anodic polarisation, due to the electrode process producing the current. The difference in the magnitude of the currents in the cathodic and anodic directions was related to the electronic structure and the ratio of the activation energies of these processes.

Odynets[63], in studying the same system, concluded that the oxide film on aluminium does not exhibit unipolar conductivity when out of electrolyte. The valve action of the $Al–Al_2O_3$–electrolyte system was attributed to a change in the rate of the electrochemical reaction taking place on the surface of the oxidised electrode during a change in the polarity.

It is evident from the experimental works on the question of the rectifying action of anodic oxide films which have been mentioned that this question is still a subject of discussion, owing to the considerable complexity of the metal–oxide–electrolyte system. The main source of the complexity is that the resistance of the body of the film in the field direction responsible for its growth is not uniform but is determined by the space charge distributed exponentially in it.

When new layers of oxide are being built up a change in the oxide modification can occur. The presence of electric fields of high potential which bring about the growth of the film can simultaneously cause structural defects. Such defects can arise from internal stresses in the film

or can be formed by the transmission of dislocations present in the metal lattice[82].

In constructing theories of the rectifying action of compact oxide films foreign scientists have used several terms: *cracks, fissure, weak spots,* and *imperfections* which imply the incompleteness of the compact structure of the film, which is responsible for the rectifying action.

This requires discussion in greater detail. The incompleteness of the compact structure of the film must be described independently of how the various authors define it. Such imperfections can be of two types: in the presence of the first we have the division of the film into two phases between which there is a third, for example, the molecules of ions of the electrolyte. In such a case the picture is one of separate centres, spots of other substances, which for various reasons can bring about conductivity in the cathodic direction and stop the current in the anodic direction.

Dislocations, *i.e.* those breaks in the periodic lattice of the oxide which lead to the appearance of acceptor or donor levels[83-85], belong to the second type of imperfections in the compact structure of the film. Such imperfections affect the electrical properties of semiconductors, since they cause the scattering of current carriers and can act as centres for the recombination and regeneration of carriers.

Dislocations can be formed by the thermal effects of the electric fields, the effect of the medium in which one crystal or another is located, etc.

It is quite probable that during the growth of the film, as its thickness increases[2] the internal stresses in a high electric field increase and imperfections of the second type are produced, which can be the cause of imperfections of the first type.

The phenomena at the metal–oxide boundary and especially at the oxide–electrolyte boundary, for example, the distribution of potential in the fixed part of the double layer at this boundary, the influence of the electrochemical reaction — all this complicates the system considerably.

All that has been written above shows the difficulty involved in the study of the rules which govern the process of film growth now under discussion and the kinetic phenomena which take place either in the film itself or at its boundaries with the metal and the electrolyte. In many instances several phenomena simultaneously affect the course of the process taking place at the boundaries and those in the body of the film.

In the development of theories to describe the current laws it is necessary to consider the relations effective at the two boundaries of the film, its semiconductive nature, and in several instances also the mechanical fractures in the structure.

All this indicates that there are still several fundamental relationships in the film which have not been revealed.

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CHEMICAL EFFECTS OF NUCLEAR TRANSFORMATIONS IN SOLIDS (CHEMICAL CONSEQUENCES OF NUCLEAR RECOIL)

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I. INTRODUCTION

Many features of the chemical processes accompanying nuclear transformations are still obscure, and far from adequately interpreted in the literature. The ever increasing number of new facts, and the difficulty of interpreting the results, which characterise studies of this type, by pointing to the weakness and contradictions of the conventional inorganic chemistry of, apparently, even the most thoroughly investigated elements, such as manganese, chromium, phosphorus, bromine, iodine, etc., stimulate new work in different branches of chemistry. Among the

problems being re-examined are disproportionation, complex formation, the stability of intermediate valencies, the reactions of polyvalent radicals with water, and many more. There is an obvious need for more detailed studies of these phenomena, and of all the stages involved in the interaction between materials; more exact models are also needed for processes which are at present only generally (*i.e.* only approximately) understood. A detailed knowledge of the chemical effects of nuclear transformations would offer deeper insight into some relatively new branches of chemistry, such as "hot atom" chemistry, solid state chemistry, radiation chemistry, etc.

No less important is the applied side of these problems: the enrichment and separation of radioactive isotopes, the production of carrier-free radioactive isotopes, the "hot" synthesis of various labelled compounds, etc.

Existing review articles in Russian deal, on the whole, with the organic aspects of this problem[1-5]. In the present article we shall be mainly concerned with chemical processes resulting from nuclear transformations in ionic crystals. We shall examine, in particular, the after-effects of nuclear reactions, with special emphasis on neutron capture reactions.

II. THEORETICAL CONCEPTS

Atoms produced in solids by nuclear reactions or by radioactive disintegration possess energy in excess of the thermal vibration energy of the crystal lattice. As a result, their chemical properties differ from those of the same atoms under normal temperature conditions. Atoms with high energy parameters have been called "hot atoms", and reactions involving such atoms have been called "hot reactions" or Szilard–Chalmers reactions (or effects).

According to their origin, "hot atoms" may possess varying degrees of excitation, which may influence their subsequent chemical fate. It may not be out of place, therefore, to discuss at this stage problems such as the magnitude of the energies acquired by atoms as a result of nuclear transformations, the origin of these excited states, and their influence on the chemical behaviour of hot atoms.

1. Nuclear Recoil as a Source of Atomic Excitation

In 1934 Szilard and Chalmers noticed[6] that radioactive iodine can be extracted by water from ethyl iodide which has been irradiated with neutrons. They ascribed the phenomenon to an "impact" effect of the neutrons, which they envisaged as a transfer of momentum from the neutron to an iodine atom, causing the radioactive iodine atom to be ejected from its parent molecule. This hypothesis was later refined by Fermi and coworkers[7], who showed that the "recoil" of the γ-quantum, produced in accordance with the law of conservation of momentum during neutron capture, is sufficient to overcome the chemical binding forces of the atom undergoing the nuclear reaction (called the recoil atom), and to convert it into a new chemical state. The magnitude of the recoil energy acquired by the hot atom depends on the type of nuclear reaction and on the mass of the recoil atom. In (n, γ) reactions the recoil energy amounts to tens or hundreds of electron-volts; in reactions causing the emission of heavy particles (including photonuclear reactions) the recoil energy can rise to tens or hundreds of kiloelectron-volts.

During radioactive disintegration, recoil energies reach the latter values only if α-particles are emitted. In β-emission, as a rule, the recoil amounts to a few eV, and in isomeric transitions or electron capture it can be as small as 10^{-2}–10^{-1} eV.

The recoil energy acquired by an atom as a result of nuclear processes is dissipated in breaking the chemical bonds holding it in the original molecule, and in imparting some kinetic energy to the excited atom. Since the energies of chemical bonds are usually of the order of a few eV, it is obvious that the majority of nuclear reactions will result in bond breaking, with the hot atom left in a "free" state. We shall be mainly concerned with cases where the recoil energy is sufficient to break chemical bonds. Radioactive disintegration processes, with the exception of α-emission, are characterised by low recoil energies which cannot rupture chemical bonds. These processes also produce hot atoms, but in this case the excitation is of quite a different type, and calls for separate detailed discussion.

2. Energy Loss Processes Available to Recoil Atoms

In 1947 Libby[8] put forward a model according to which the recoil atom loses its kinetic energy exclusively as a result of elastic interactions with lattice atoms, the interactions being treated as collisions between billiard balls (rigid spheres). Libby's model requires the acceptance of the following propositions[4]: (a) the energy of the recoil atom is set free after a few collisions with lattice atoms, over a path amounting to a few Ångstrom units; (b) the sudden evolution of a large amount of energy (up to several keV) raises the temperature, locally, to 10^6–10^7°K, causing melting and partial intermingling of the material in a volume comprising $\sim 3 \times 10^5$ atoms; (c) the molten region exists for a time of about 10^{-8} s, and this is sufficient for thermal equilibrium to be established and for many chemical processes to occur in the molten region, since the normal lattice vibration period is $\sim 10^{-13}$ s; (d) in view of the high mobility and of the disorder of the atoms in the melt, we can expect lattice atoms originally quite remote from the recoil atom to influence its chemical fate; (e) the distribution of recoil atoms over various chemical forms must be in keeping with the initial recoil energy of the hot atom, *i.e.* with the type of nuclear reaction.

Without rejecting Libby's model outright, we may suggest that Harbottle and Sutin's model[9] of the "hot" zone is more consistent and well-founded. It is firmly based on the concepts of solid-state physics[10-13] derived from the work of Seitz and Koehler, and concerned with the motion and retardation of charged particles in a crystal lattice.

The hot atom, endowed with some kinetic energy, will penetrate a certain distance through the solid, losing its energy as a result of interactions with the surrounding medium. The nature of the interaction varies continuously during the atom's excursion, since it is in some way related to the kinetic energy.

All the collisions suffered by the atom can be divided into two categories: elastic collisions and inelastic collisions. Elastic collisions are those in which the total kinetic energy of the moving and the fixed atom is conserved; inelastic collisions are characterised by a loss of kinetic energy, resulting from electronic excitation and ionisation.

Whereas the only role of the electrons in elastic atomic collisions is to screen the nuclear charges to a greater or lesser extent, in inelastic collisions the moving atom interacts directly with an electron of the target atom, promoting the electron to an excited state, or even dislodging it from its orbital, and thus causing ionisation of the medium along the track of the recoil atom. Similarly, electrons of the recoil atom are extracted from their orbitals by the electrostatic field of the target atoms, and the moving atom can thus be freed of all or some of its outer electrons. Direct interactions of this kind between atoms and electrons are, of course, only possible when the recoil energy is large and the orbital velocity of the electrons is comparable with the velocity of the recoil atom. Seitz [10] gives the following expression for the limiting kinetic energy leading to ionisation, E_i:

$$E_i = \frac{1}{8}\left(\frac{M}{m}\right)\varepsilon_i, \qquad (1)$$

where M and m are the masses of the recoil atom and of the electron respectively; ϵ_i is a quantity of the same order as the energy gap between the valence band and the conduction band for the case of ionisation of the target atoms. If we are interested in the possibility of ionisation of the neutral recoil atoms, we equate the energy term ϵ_i to the ionisation potential of the recoil atoms in the gaseous state. Limiting ionisation energies for recoil atoms of different masses are set out in Table 1.

If the energy of the recoil atom is $E \geq E_i$, it is dissipated mainly in the ionisation and excitation of electrons from the target and the moving atom. When the recoil energy drops to $E < E_i$, ionisation ceases, but electron excitation can still take place, because exciton energies are lower than the corresponding ionisation energies, and the limiting excitation energy is several times lower than the limiting ionisation energy E_i. Lastly, if the energy of the recoil atom is less than the limiting excitation energy, the electron clouds begin to react adiabatically on the close approach of atoms, and all further energy losses by the moving atom occur *via* elastic collisions with lattice atoms. The electrons set free in the early stages may be collected by the recoil atom as long as the latter's electron affinity remains higher than the ionisation potentials of the lattice atoms.

We must distinguish two energy regions in which a moving atom can lose energy as a result of elastic collisions: the Rutherford scattering region and the region of scattering according to the laws of rigid spheres.

The main difference between the two kinds of collision lies in the different degrees of screening of the nuclear charges by the electron clouds. In the Rutherford region, corresponding to a high kinetic energy of the recoil atom, there is deep mutual penetration of the electron clouds, *i.e.* small screening of the positive nuclear charges. When a "rigid sphere" impact takes place, on the other hand, the mutual repulsion of the electron shells exceeds the kinetic energy of the moving atom. Under these conditions the electron shells do not interpenetrate, and screening is complete. It is obvious that the transition from one kind of scattering to the other takes place gradually, as the moving atom loses kinetic energy, and that there must be a fairly wide intermediate energy region within which neither mode of scattering occurs to the complete exclusion of the other.

TABLE 1. Limiting ionisation energy of neutral recoil atoms

Recoil atom	Atomic weight	ϵ_i, eV	E_i, keV
C	14	11.26	36.06
P	32	10.55	77.65
Co	60	7.86	109.17
Br	80	11.84	217.86
I	127	10.44	304.9

It follows directly from the absence of screening that collisions of this type between two atoms, in which a significant fraction of the energy of the moving atom is transferred to the lattice atom, must have a small effective cross-section. If the energy given by the collision to an atom of the medium exceeds the threshold displacement energy E_d, estimated as 25–30 eV, the elastic collision will displace the stationary atom from its crystal lattice site. If energy considerably in excess of E_d is transferred during the collision, the displaced atom produces secondary displacements, which give rise to a whole shower of displacements.

It can be shown that in the Rutherford scattering region the effective cross-section for displacement, σ_d, is smaller than the geometrical dimensions of the atoms, leading to a large mean free path (~ 100 Å) of the recoil atom between collisions able to displace lattice atoms.

As the atom slows down, and its store of kinetic energy decreases, the effective cross-section for displacement σ_d increases, and reaches a maximum in the region where collisions occur by the rigid sphere mechanism. The free path of the recoil atom correspondingly decreases, tending towards the interatomic distance.

To discuss this problem in greater detail, we must introduce the concept of the "temperature spike". [10,11] The temperature spike is a well defined region within the solid, in which the amount of energy scattered is sufficient to heat the atoms above the temperature corresponding to the normal thermal vibrations of the lattice (~ 0.03 eV). The dimensions, lifetime, and maximum temperature of this hot region are a function of the amount of scattered energy and of the thermal conductivity of the medium.

We can distinguish two types of temperature spike: "displacement spikes" and "thermal spikes". The difference between them is that more energy is scattered in the former, this energy being introduced mainly through a chain of displacements triggered off by the recoil atom. This leads to fusion and mixing of the material in the displacement spike, which includes (according to Brinkman [14,15]) several thousands of atoms. After a short time (a few tens or hundreds of lattice vibrations) the displacement spike cools down and "freezes", and the displaced atoms which have not been able to find correct lattice positions are quenched into a state of complete disorder.

If the energy transferred to a lattice atom is insufficient to cause a chain of displacements, and only few atoms are expelled from their sites, the region is called a "thermal spike". A thermal spike is formed also when the energy transferred to a lattice atom by a collision is less than the threshold energy for displacement, E_d. In this case the excitation is conveyed to the surrounding crystal lattice by large-amplitude vibrations of the lattice atom having suffered the collision, which cause vibrational excitation of other particles of the solid. Both phenomena (thermal spike and vibration spike) are analogous to the rapid heating

of a confined volume to a high temperature (sufficient to "melt" 5–10 atoms), followed by rapid cooling as the heat diffuses into the bulk of the crystal.

Displacement spikes and thermal spikes appear all along the track of a recoil atom, as though they were "branching off". In the Rutherford scattering region the temperature spikes are fairly well spaced out (~ 100 Å), and do not form a continuous damaged region. As the recoil atom slows down, it begins to interact with the material at shorter intervals, and after a short time the individual spikes begin to merge. The time required for the excited regions to coalesce in this way is determined by the thermal conductivity of the medium.

By the time the atomic interaction takes the form of collisions between hard spheres the recoil atom has lost most of its initial energy, which becomes scattered over a track of appreciable length (~ 1000 Å) originating where the hot atom was produced. It is in this respect that the conclusions of Seitz and Koehler's review[10] differ most significantly from Libby's model, which requires that the whole of the kinetic energy of the recoil atom, whatever its magnitude, shall be dissipated in a track no more than ~ 10 Å long. This can only be true if the recoil energy is low, when Libby's and Seitz and Koehler's models give identical results. It seems probable, therefore, that Libby's model is a special case of the Seitz–Koehler theory.

It can be shown mathematically that atomic collisions of the hard sphere type have an effective displacement cross-section very close to the geometrical cross-sections of the atoms, and that the mean free path approximates to the interatomic distance[12,13]. In this case the recoil atom must dissipate the last few hundred eV of energy in a few thermal spikes situated close together in the crystal. The distance between these spikes is so small (of the order of the interatomic distance) that after a very short time (a few vibration periods of the lattice atoms) the spikes merge into a single excited region which Harbottle and Sutin have termed the "hot spot".[9] This view of the formation of a hot zone in which the recoil atom is arrested ("sticks") was put forward by the authors in order to describe the chemical behaviour of recoil atoms in solids.

We shall now discuss some quantitative characteristics of the hot zone.

3. Parameters of the Hot Zone

We shall consider the most typical nuclear reaction, the n,γ reaction, in which the recoil atom dissipates an energy of ~ 300 eV in the hot zone. We have to determine the number of displaced atoms in a thermal spike of this energy. If $\nu(E)$ is the average number of atoms displaced by an atom of energy E, and $2E_d < E < E_i$, we find both theoretically and experimentally that

$$\nu(E) = \frac{E}{2E_d}, \qquad (2)$$

where E_i is the limiting ionisation energy.

The physical significance of Eqn. (2) is not difficult to see: on the average, one-half the energy of the moving atom goes to produce displacements, each displacement accounting for an energy E_d, whilst the other half of the energy is scattered by collisions in a region below the threshold energy, causing high-frequency phonons to appear in the lattice.

Thus, in a hot zone of energy 300 eV we find 5–6 atoms displaced from their normal sites ($E_d \simeq 25$ eV), which have enabled the recoil atom to dissipate its residual kinetic energy by collisions and come to a halt. The sudden loss of energy in a very short time (~ 10^{-13} s) causes a local rise in temperature, given as a function of time t and distance r from the centre of the zone by the expression

$$T(r, t) = \frac{Q}{2\pi^{3/2}cd} \times \frac{1}{(Dt)^{3/2}} \exp\left(-\frac{r^2}{4Dt}\right), \qquad (3)$$

where c is the specific heat, d the density, D the thermal diffusivity (taken as ~ 0.001 cm² s^{-1}), and Q is the energy given out by the recoil atom in the hot zone.

Eqn. (3) assumes that the whole of the energy is evolved in a time of ~ 10^{-13} s at the centre of the hot zone, and diffuses away with spherical symmetry. The ratio $r^2/4D$ has the dimensions of time, and characterises the propagation of heat in the zone. At time t, and distance

$$r = \sqrt{4Dt} \qquad (4)$$

from the centre of the zone, the temperature has dropped by a factor of e.

The heat liberated by the hot atom is sufficient to heat ~ 1000 atoms of the crystal lattice to above the melting point. If the melting point is T_m = 1000°K, and the energy expended in melting is $Q \simeq 300$ eV, we have

$$\frac{Q}{3kT_m} \simeq 1000,$$

and the radius of the hot zone, r_m, is ~ $10r_s$, where r_s is the atomic radius, and can be found from the relation

$$\frac{4}{3}\pi r_s^3 = \frac{1}{n_0},$$

n_0 being the number of atoms in 1 cm³.

From Eqn. (4), assuming a value of $D \simeq 0.001$ cm² s^{-1}, we can calculate the time for the spherical thermal spike to spread over this region, of radius $r = 10r_s$ (~ 15 Å). The result is approximately 6×10^{-12} s. It readily follows from Eqns. (3) and (4) that after 2×10^{-11} s the radius of the hot zone is 30 Å, and the mean temperature has fallen to 150°. Since by this time the hot zone has effectively ceased to exist, its lifetime works out at about 10^{-11} s, and the volume heated beyond the melting point comprises about 10^3 atoms.

The statement that the material has been heated to above its melting point describes the degree of thermal excitation in the hot zone, but does not necessarily mean that the material has achieved the amorphous structure of a true liquid, because the spreading time (6×10^{-12} s) of the thermal energy in a region of radius $r_m = 10r_s$ is comparable with only a few tens of atomic vibration periods, and is therefore too short to allow the establishment of full thermal equilibrium. Since the temperature of this region rises extremely rapidly, and owing to the influence of the surrounding medium, it is probably best to think of the hot zone as a superheated solid, though melting may actually take place at the very centre.

4. Reactions in the Hot Zone

The highly activated atoms to be found during the lifetime of the hot zone can undergo chemical reactions which are precluded for those same reactants under normal energy conditions. These so-called "hot" reactions do not

depend on the temperature of the medium, and give rise to products which cannot form at thermal energies.

One type of hot reaction is the replacement of a lattice atom by the moving atom upon collision, a process which does not increase the overall number of displaced atoms. Replacement must occur[16,17] if the energy transferred to the target atom is greater than E_d, whilst the recoil atom after collision has an energy less than E_d. This is closely akin to the fluid reaction cell model proposed by Franck and Rabinowitsch[18] and developed by Libby[8,19] and by Miller *et al.*[20]

Replacement will take place also if an atom acquires an amount of energy lying between E_p and E_d (where $E_p < < E_d$), whilst the kinetic energy retained by the moving atom is less than E_d. In this case the recoil atom remains at a vacant lattice site. Kinchin and Pease[21] have estimated a ratio $E_d/E_p \simeq 10$ for alloys, and calculated that 4.7 replacements occur for each displacement. This means that something like 5 out of 6 recoil atoms are captured by the original molecule if all the atoms are identical. In a system containing atoms lighter than the recoil atoms, the proportion of displacements is much higher than 1/6.

We need not confine our attention to reactions resulting from purely mechanical effects: we should also consider typical chemical processes occurring in the localised high temperatures of the hot zone. Due to the high temperature, to the radiation, and to the displacements generated by the moving atom, molecules in the hot zone are dissociated and decomposed with formation of charged or neutral radicals, residues, and recoil fragments. Thus the breaking of the original chemical bonds, the formation of new bonds, the recombination of free radicals, charge transfer effects, and the distortion of electronic structures are the phenomena most likely to occur during the lifetime of the hot zone. Reactions between a recoil fragment and the parent molecule (the so-called ion–molecule reactions), exchange reactions, and diffusional jumps by interstitial or vacancy mechanisms are also possible.

We must now consider the extent to which these reactions can proceed in the short time of $\sim 10^{-11}$ s, *i.e.* during the lifetime of the hot zone. The frequency ν of a chemical process whose free energy of activation is F is given by the expression

$$\nu = \nu_0 e^{-F/kT}, \tag{5}$$

where ν_0 is the frequency factor, equal $\sim 10^{13}$ s^{-1}.

Integration of this expression gives n_j, the number of times the process occurs at the centre of the hot zone:

$$n_j = \int_{t_0}^{\infty} \nu_0 e^{-F/kT(t)}\, dt, \tag{6}$$

where $T(t)$ is obtained from Eqn. (3). For crystals which obey Dulong and Petit's law for lattice vibrations, Seitz and Koehler give the solution

$$n_j = 0.095 \frac{\nu_0 r_s^3}{D} \left(\frac{Q}{F}\right)^{2/3}. \tag{7}$$

For the reaction between a given fragment and another strictly defined fragment, taking Q = 300 eV and F = 1 eV, we find $n_j \simeq 4$. On the other hand, if our fragment is allowed to react with any other fragment, we find $n_j = 4\eta$, where η is the number of independent paths by which the reaction can occur.

Studies of the thermal and radiation-induced annealing of recoil atoms in solids have shown that all these processes do not by any means go to completion during the lifetime of the hot zone. Some of the processes are quenched at some intermediate stage, and additional energy has to be supplied to the system (*e.g.* by annealing) to allow the chemical reaction to proceed. The following effects may cause reduced yields:

a. The fragments are not nearest neighbours, and diffusion in the hot zone is necessary in order to bring them together.

b. As pointed out by Seitz and Koehler, Eqn. (5) applies only to simple atomic crystals. Systems used in studies of the Szilard–Chalmers reactions, which have as a rule a more complicated structure, involve steric factors not considered in Eqn. (5). In such systems Eqn. (5) must be replaced by an equation of the type

$$\nu = \left(\frac{kT}{h}\right) e^{\frac{\Delta S^{\neq}}{k}} e^{\frac{\Delta H^{\neq}}{kT}}, \tag{8}$$

in which the entropy of the activation term, $e^{\frac{\Delta S^{\neq}}{k}}$, allows for steric and other probability factors, the universal frequency $\frac{kT}{h}$ replaces ν_0, and the quantity $\Delta H^{\neq}$ is identified with the activation energy.

It is clear that the quantity $n_{\neq}$ indirectly determines the probability of the process occurring during the lifetime of the hot zone. This probability is higher the lower the activation energy of the process. Thus, for low activation energies of no more than a few eV there is an appreciable probability of reaction between the recoil fragment and its nearest neighbour. When the substance irradiated is pure, the nearest neighbour is nearly always a molecule of the parent compound, which suggests that ion–molecule reactions (*e.g.* exchange reactions) may play an important role during the existence of the hot zone. Such reactions may well be responsible for the wide variety of products obtained from nuclear transformations. This view was put forward by Harbottle and Sutin[9], in contrast to Willard's claim[22] that the multiplicity of products resulting from Szilard–Chalmers reactions can be ascribed to random bond breaking along the track of the recoil atom. Harbottle and Sutin's objection to this theory stems from the low concentration ($\sim 10^{-2}$) of free radicals along the path of the moving atom.

III. METHODS OF STUDYING THE CHEMICAL STATE OF RECOIL ATOMS IN CRYSTALS

The atoms resulting from various nuclear reactions are present, as a rule, in vanishingly low concentrations in the target crystal, and their determination by other than radiochemical methods is extremely difficult.

The isotopic carrier method–one of the commonest procedures — enables the conventional operations of semimicro quantitative analysis, such as precipitation, extraction, etc, to be applied to the study of radioactive atoms. The shortcoming of this method is the lack of suitable carriers for unstable forms of the recoil atoms, exhibiting intermediate valencies. The existence and chemical state of such intermediate forms must be guessed from various indirect considerations. Information of this kind may be obtained from studies of the changes suffered by the recoil atoms during thermal or radiation-induced annealing of the irradiated crystals.

Thermal annealing as a method of investigation has the advantage that the crystal returns to its initial unexcited state, the energy required for the conversion being a measure of the depth of the metastable energy levels of the recoil atoms (or, in general, of the lattice defects), and also of the activation energies of the relevant processes. Furthermore, any form of annealing may be followed by monitoring various physicochemical properties of the irradiated specimens, whence conclusions may be drawn regarding the nature and the underlying causes of the observed phenomena.

More accurate results can be obtained by chromatography or electrophoresis in the absence of carriers. These methods often given unambiguous indications of the existence of recoil atoms in unstable chemical forms, but the interpretation of the chromatograms and histograms still presents serious difficulties. Furthermore, these methods presuppose high specific activities of the target materials, which are not always available to the experimenter.

Clearly, dissolution of the target as a preliminary to any form of radiochemical analysis can bring about a significant perturbation of the distribution of a radioactive isotope among various chemical states, as compared with the original distribution in the crystal. It would be very desirable, therefore, to have some physicochemical method of analysis which did not require conversion of the crystal into a liquid phase.

In the study of radiation damage in solids valuable information on structural defects and on the presence of unstable radicals in the lattice can be deduced from optical, electrical, and magnetic measurements. But since the radioactive atoms are present at very low concentrations, lower than the concentrations of radiation-induced defects by several orders of magnitude, it has not yet been found possible to study radioactive atoms by these procedures. Some information can be derived from experiments on the diffusion of radioactive atoms in the irradiated solid specimens at high temperatures, with and without externally applied electric fields[23-26]. Unfortunately, these experiments offer little concrete evidence as to the initial chemical state of the radioactive atoms, because the high temperatures involved can affect the relative amounts of radioactive atoms in different valency states.

The study of chemical processes induced by various kinds of radioactive disintegration rather than by nuclear reactions offers a wider choice of techniques. For example, the state of daughter atoms in the gas phase can be conveniently studied by collecting the recoil ions by means of an electric field or mass-spectrometrically. In solids, the Mössbauer effect has been used to study various unstable complexes formed during β-disintegration by a daughter atom in the crystal lattice. One section of the present review is specially devoted to the Mössbauer effect.

The retention† of activity after recoil in each of the various chemical forms provides the basic quantitative characterisation of the chemical effect of recoil. Existing methods of investigation depend on monitoring the final products by means of radioactive atoms, and do not give any information on the nature of the *primary* recoil fragments. Hence, present-day studies of these processes are confined to measurements of retention and of its dependence on various factors, which are variously combined to give the final result. We shall now discuss the most important factors, and the main principles which have been deduced from experimental results on retention in various chemical systems.

IV. BASIC EXPERIMENTAL RESULTS AND THEIR INTERPRETATION

1. Dependence of Retention on the Chemical Nature of the Recoil Atom and of Its Environment

We have already remarked that a recoil atom can become ionised at a given point in its path if its kinetic energy is in excess of the limiting ionisation energy E_i, which is measured in tens or hundreds of keV, and depends on the ionisation potential and mass of the recoil atom. Ionisation of this kind can occur in any crystal, whatever its structure. The more complicated ionic crystals, comprising complex ions, can show ionisation of another kind. In these materials ionisation sets in even at low recoil energies: in (n, γ) reactions, for example, when the bond between the complex-forming ion (recoil atom) and its ligand groups is broken. According to Libby[19], this process involves the following mechanism.

In (n, γ) reactions, the velocity of the recoil atom is so much lower than the orbital velocities of the electrons that the latter may have time to take up a configuration of minimum free energy between the central atom and its surroundings. The final distribution of the electrons during fission of the bonds between the complex-forming ion and its ligands will depend on their relative electron affinities. If the complex-forming ion is highly electropositive, and the ligands are highly electronegative, there is a high probability of finding the electrons on the substituents, whilst the central ion is expelled from its surroundings bearing a multiple positive charge. Under these conditions, the charge on the recoil atom will be higher the greater the number of ligands lost due to recoil.

In his study of the chemical state of radio-manganese in potassium permanganate[19], Libby suggested (in conformity with his hypothesis) that a whole series of radio-manganese fragments, bearing different charges, is formed: MnO_3^+, MnO_2^{3+}, MnO^{5+}, Mn^{7+}. An analogous series can be postulated for chromium in neutron-irradiated potassium chromate: CrO_3, CrO_2^{2+}, CrO^{4+}, Cr^{6+}, and for rhenium in potassium perrhenate: ReO_3^+, ReO_2^{3+}, ReO^{5+}, Re^{7+}.

Since in Libby's model the central ion does not change its valency during recoil, it could be thought that the retention must always be 100%. This is not so, however, because the fragments formed during recoil may react in different ways with water during the subsequent dissolution, depending on their respective oxidation potentials[27]. Thus, the series CrO_3, CrO_2^{2+}, CrO^{4+}, Cr^{6+} forms a sequence in which the oxidation potential and the tendency towards reduction increases from left to right.

It is known that CrO_3 and CrO_2^{2+} (the chromyl ion) are hydrolysed by water to chromate at all pH values, but are not reduced by water to lower valency states. The other radicals oxidise water, and are reduced to Cr^{III}. The

† The term "retention" is widely used in the literature. Qualitatively, it denotes the occurrence of radioactive atoms in a given chemical form; quantitatively, it denotes the percentage of radioactive atoms in that form. As used in the present review, it refers invariably to retention in the parent compound.

reactions of the chromium residues during dissolution are of the form

$$\left.\begin{aligned} CrO_3 + H_2O &\rightarrow CrO_4^{2-} + 2H^+ \\ CrO_2^{2+} + 2HO^- &\rightarrow CrO_4^{2-} + 2H^+ \end{aligned}\right\} \quad (9)$$

or

$$CrO^{4+} + H_2O \rightarrow Cr^{3+} + O_2 + 2H^+. \quad (10)$$

Thus, retention will be a function of the relative numbers of the various recoil fragments. Table 2 shows the retention of chromium, manganese, and halogens in different compounds irradiated by neutrons at room temperature (neutron capture reaction with γ-emission).

The relatively high retention (60–70%) in chromates can be explained by the above considerations. The CrO_4^{2-} anions must pass, during recoil, through three forms before giving a form capable of oxidising water. On the other hand, oxy-anions of higher oxidation potential need to be taken through fewer states of oxidation to give a form which oxidises water. Hence, high oxidation potentials of the ion correspond to low retention of the recoil atom in its upper oxidation state. This is shown graphically in Fig. 1, which is based on Harbottle and Sutin's experimental results[36].

Further confirmation of this model could be obtained from systematic studies of retention in the oxy-salts of a given element in different oxidation states (*e.g.* potassium permanganate and manganate, etc.). Work of this type is now in progress[37].

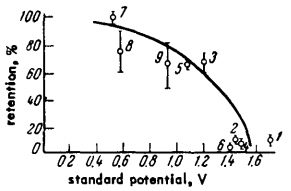

Fig. 1. Relationship between retention in neutron-irradiated crystalline salts and their oxidation potentials:
1) permanganate; 2) bromate; 3) chromate; 4) chlorate; 5) iodate; 6) periodate; 7) perrhenate; 8) arsenate; 9) iridate.

It should be noted that the behaviour of oxy-anions in Szilard–Chalmers processes is different from their behaviour towards radiolysis or thermal decomposition. Thus, radiolysis by electrons and thermal decomposition of permanganate give rise[38] to lower valency compounds: Mn^{VI}, Mn^{V}, Mn^{IV}. No such effect is observed in Szilard–Chalmers reactions.

What is the nature of the reactions which occur under conditions of high local temperature? The track of the recoil atom in an (n, γ) reaction usually amounts to a few lattice constants, and a small displacement from the fragments of the original molecule enables such an atom to recombine with oxygen ions, thus:

$$CrO^{4+} + O^{2-} \rightarrow CrO_2^{2+}. \quad (11)$$

We can also postulate activated exchange of oxygen ions between the recoil fragment and a neighbouring CrO_4^{2-} ion (the so-called ion–molecule reaction[9]):

$$\left.\begin{aligned} Cr^{*6+} + CrO_4^{2-} &\rightarrow Cr^{*}O^{4+} + CrO_3 \\ Cr^{*}O^{4+} + CrO_4^{2-} &\rightarrow Cr^{*}O_2^{2+} + CrO_3 \end{aligned}\right\}, \quad (12)$$

or

leading, of course, to increased retention. If we assume that the Cr^{*6+} ion produced by radioactive recoil can take up oxygen atoms from the surrounding crystal lattice, the last two reactions can be envisaged as occurring consecutively during the excursion of the chromium atom through the thermal spike. The activation energy for the transfer of oxygen is of the order of 3 eV. Thus we can calculate that oxygen transfer may occur several times during the lifetime of the hot zone[36]. Experiments on solid solutions of potassium chromate and fluoroberyllate[39,40] also provide some indirect evidence of the reality of these reactions (see below).

Evidently, a different situation will exist when the central complex-forming ion has an electronegativity comparable to that of oxygen, as in the case of the halogens. Here the oxygen may come away from the halogen leaving its electrons on the latter, and thus lower its valency. The effect will be strongest with chlorine, and less marked with iodine. The result will be to form the radicals XO_4^-, XO_3^-, XO_2^-, XO^-, and X^-, (where X is a halogen atom), which react with water to give the corresponding acids.

TABLE 2. Retention values for various compounds.

Compound	Recoil atom	Retention, %	Literature reference	Compound	Recoil atom	Retention, %	Literature reference
Li_2CrO_4	Cr^5	66	28	$Ca(MnO_4)_2 \cdot 5H_2O$		6.0	
$Li_2Cr_2O_7$		54.5		$NaClO_3$	^{38}Cl	1.5	7, 19
Na_2CrO_4		74		$NaClO_3$		3.5	30
$Na_2Cr_2O_7$		80		$NaClO_3$	^{38}Cl	12.5	31, 32
K_2CrO_4		61		$NaClO_4$	^{38}Cl	0	
$K_2Cr_2O_7$		90		$KClO_3$		3.5	
$(NH_4)_2CrO_4$		17.5		$KClO_4$		0	
$(NH_4)_2Cr_2O_7$		32		$KClO_4$	^{38}Cl	2.2	32
$Na_2CrO_4 \cdot 4H_2O$		88		$LiBrO_3$	^{82}Br	8.0	33
$Na_2Cr_2O_7 \cdot 2H_2O$		73		$NaBrO_3$		11	
$MgCrO_4$		55		$KBrO_3$		11	
$ZnCrO_4$		35		$RbBrO_3$		13	
CrO_3		78		$CsBrO_3$		12	
$AgMnO_4$	^{56}Mn	8.0	29	$AgBrO_3$		15	
$LiMnO_4$		8.8		$Ba(BrO_3)_2$	^{80m}Br	9	33
$NaMnO_4$		9.1		$LiIO_3$	^{128}I	66	34
$KMnO_4$		22.5		$NaIO_3$		67	
$Ca(MnO_4)_2$		6.0		KIO_3		67	
$Ba(MnO_4)_2$		12.8		NH_4IO_3		22	
$NaMnO_4 \cdot 3H_2O$		6.9		$KHIO_3$		53	
$LiMnO_4 \cdot 3H_2O$		4.0		KIO_4		4.0	35

The following distribution of radio-iodine among the various chemical forms has been observed[34] after neutron irradiation of iodate and periodate solutions:

$$IO_3^- + n \rightarrow \begin{vmatrix} IO_3^- & 6\% \\ IO_2^- & 34\% \\ IO^- & 54\% \\ I^- & 6\% \end{vmatrix} \qquad IO_4^- + n \rightarrow \begin{vmatrix} IO_4^- & 6\% \\ IO_3^- & 28\% \\ IO_2^- & 60\% \\ IO^- & 6\%. \end{vmatrix} \qquad (13)$$

In both cases the loss of two oxygen atoms appears to be favoured. However, we must also consider at least two other factors, which can influence the relative abundance of the various fragments: (1) the mass of the halogen atom affects the recoil energy and therefore also the number of atoms lost and the extent to which the recoil fragment is reduced; (2) the enthalpy of formation of the XO_3^- ion governs the tendency towards reduction or decomposition of the parent molecule. Note that ΔH° values for IO_3^-, BrO_3^-, and ClO_3^- are -55, -9.6, and -23.5 kcal mole^{-1} respectively[41].

Under the combined influence of these three factors retention in (n, γ) reactions decreases, as expected, from iodine to chlorine. It amounts to 67% for $NaIO_3$,[34] 11% for $NaBrO_3$,[33] and 12.5% for $NaClO_3$.[31,32] From this point of view, Vlatkovic and Aten's results[42] on the chemical state of chlorine in KIO_3 crystals are not difficult to understand. The chlorine, produced from potassium by an (n, α) reaction, was found exclusively in the chloride fraction.

This picture, based on Libby's model[19], is probably a coarse approximation, and ignores other possible processes. For example, the results of electron paramagnetic resonance measurements[43] on V-centres in $KClO_3$ crystals irradiated with X-rays point to the presence of ClO radicals covalently bound to ClO_3^- ions. The authors also postulate the presence of the O_2^- molecule-ion. The presence of the oxide Cl_2O_6, and of a small amount of ClO_2 and ClO_4^-, was deduced from studies of the optical absorption spectra[44] of of potassium chlorate irradiated with X-rays. In the KIO_3 crystal lattice, on the other hand, neutral radicals of the type IO and IO_2 are most likely to be formed. Studies have been made also of the influence on the retention of the pH of irradiated iodate solutions and of the nature of the medium used to dissolve irradiated crystals. The retention has been investigated also as a function of the presence of various oxidising agents in the solution being irradiated (oxidants do not affect the retention when added after irradiation of the solution). From all this work it appears that compounds showing various valencies, or unstable radicals tending to disproportionate or to exchange, can be formed during recoil[34]. This tendency can have a profound influence on retention in crystalline halogen oxy-salts.

In spite of the large number of processes which may accompany nuclear recoil, simplifications such as Libby's model of the ionisation of recoil fragments[19], are very convenient at certain stages of the investigation, since they go a long way towards surmounting the difficulties of interpreting phenomena as complicated as the Szilard–Chalmers reaction.

2. Influence of the Cation upon Retention Processes

This effect is appreciable only in the case of the ammonium ion (see Table 2). Harbottle ascribes[36] the decrease in retention to the reducing action of hydrogen in the hot reactions between recoil fragments and the ammonium ion.

The salts of Group II elements also show a lower retention than the corresponding salts of the alkali metals. The reducing action in this case is probably a consequence of the high ionisation potentials of divalent metals. Their stronger electrostatic field promotes the disintegration and rearrangement of excited molecules. Metal oxide molecules, containing oxygen, may be formed under these conditions: this would hinder reactions of type (11), and lower the retention. The alkali metals must have a similar effect, but it is difficult to distinguish between them because of the smaller difference in ionisation potentials.

The stability of permanganates towards thermal decomposition (which can be visualised as retention in the form of the parent substance) also increases in the sequence[45] Ag^+, Li^+, Na^+, K^+, Rb^+, Cs^+, and Mg^{2+}, Ba^{2+} for the case of divalent metals (*cf.* the results of Table 2).

It is difficult to discern any correlation between the results of retention measurements and crystal density, concentration of oxy-anions in the solid phase, or crystal lattice structure. Obviously, these factors play a minor role as compared with those which, to a first approximation, control the chemical processes attending the recoil phenomenon.

3. Influence of the Degree of Complexity and of Homogeneity of the Ligands. Steric Effect

Baumgärtner and Zahn[46] have studied the retention of radioactive chromium in (n, γ) reactions involving the chromium complexes $Cr(Bz)_2$, $(Bz)Cr(CO)_3$, $Cr(CO)_6$, $Cr(Ms)_2$, $Cr(\psi - C)$, where Bz = benzene, Ms = mesitylene, and $\psi - C$ = pseudo-cumene. They were unable to detect any correlation between retention and the mass, the number, or the heat of formation of the ligands. The retention was 12% for $Cr(Bz)_2$, 9% for $(Bz)Cr(CO)_3$, 60–70% for $Cr(CO)_6$, 4.5% for $Cr(Ms)_2$, and 4.5% for $Cr(\psi - C)$.

Nor can the results be explained on the basis of the ligand–central atom bond energy alone, since these bonds are more stable in the last two compounds, and retention in these systems should amount to more than 12%.

It seems highly probable that the author's failure to demonstrate a correlation is due to the presence of some other, more powerful influence, rather than to a complete lack of connection between retention and these particular properties. Such an effect could arise as follows: the probability of regenerating the original molecule, partly disintegrated by the radioactive recoil, decreases with increasing structural complexity of the ligand molecule, and also if the ligands are not of a single kind, since the number of possible chemical forms produced by the decomposition of a few molecules by recoil now becomes very large. The latter effect can be demonstrated for inorganic compounds (*e.g.* thiosulphates).

The additional loss of retention shown by the last two compounds may be due to their large molecular masses, which give rise to steric hindrance opposing the return of the recoil atom towards its original position. A similar explanation has been advanced[47], on the basis of the steric effect, to account for the sharp decrease in retention accompanying the addition of pyridine ligands to Zn, Co, and Cu phthalocyanines.

Among inorganic crystals, the steric effect is very clearly shown by mixed crystals of potassium chromate and fluoroberyllate[39,40]. At the 1% level of potassium chromate

concentration the retention is reduced from 60–70% (for pure chromate) to 25–30%, and is found empirically to obey the law

$$R_0 = 30 + 0.4x, \qquad (14)$$

where R_0 is the retention and x is the percentage of chromate. Clearly, in these mixed crystals the molecules of potassium fluoroberyllate play no part in the chemical processes. As stated above, the hot-zone process leading to increased retention in chromates consists either in recombination of the recoil fragment with the residues of the original oxy-anion, *i.e.* with oxygen anions, or in reactions between multiply charged chromium recoil ions and the oxygen of stable oxy-anions. Probably, these processes may become inhibited, or even precluded, in mixed crystals for purely geometrical reasons.

4. Isotope Effect of Recoil

This effect is unmistakably observed with elements whose isotopic composition enables the Szilard–Chalmers reaction to be studied simultaneously on more than one radioactive isotope. The phenomenon depends on the slight difference in chemical behaviour between different isotopes of a given element during the lifetime of the hot zone or during the subsequent annealing of radiation damage. There is as yet no convincing interpretation of this complicated phenomenon in the literature.

In alkali metal bromates[33] (with the exception of lithium) retention is the same for both ^{82}Br and ^{80m}Br. However, the two isotopes behave differently during annealing. The retention of the heavier isotope increases faster, and reaches a higher plateau, as shown in Fig. 2. For $LiBrO_3$ the situation is reversed: the initial retention is smaller for ^{82}Br, but on heating, the curves for the two isotopes merge after two hours (Fig. 3).

Maddock and coworkers[48] have reported a considerable isotope effect in neutron-irradiated sodium hexachloroiridate: the retention was 47% for ^{192}Ir and 40% for ^{194}Ir. More refined analytical techniques[49] gave a retention of 20.9% for ^{192}Ir and 17.3% for ^{194}Ir in K_2IrCl_6, and 5.7% for ^{192}Ir and 2.8% for ^{194}Ir in $(NH_4)_2IrCl_6$.

An analogous isotopic difference for rhenium was observed by Apers and Maddock[50]. In K_2ReCl_6 crystals the proportion of heptavalent rhenium was found to be 32.8% for ^{188}Re, and 36% for ^{186}Re (Re^{IV}: 63% and 59% respectively). The rates of thermal and radiation-induced transformations were practically identical for the two isotopes, and the annealing graph consists of two curves which do not coalesce. It has been shown experimentally[51] that the

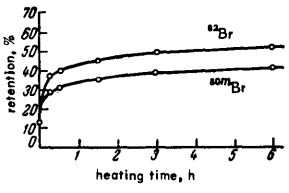

Fig.2. Difference in behaviour of bromine recoil isotopes during annealing at 200° in $RbBrO_3$.

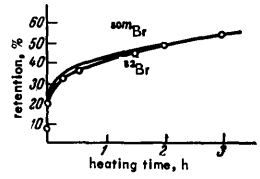

Fig.3. Difference in behaviour of bromine recoil isotopes during annealing at 200° in $LiBrO_3$.

retention of rhenium is unaffected if fast neutrons are used for the nuclear reaction. Thus the effect cannot be easily explained on purely energetic grounds. A study of the gamma-capture spectra and of the conversion coefficients of both isotopes may help to clarify this complicated phenomenon.

Conclusions as to isotopic differences in retention reached by comparing data for different nuclear reactions must be treated with greater caution; the same is true of work in which any one author has examined only one isotope of a given element. Comparative studies of retention for the different isotopes are essential in this case, since differences may arise in the irradiation of the target, in the analytical method used, and in the subjective skill of the experimenter. All these can have a profound effect on the final result.

For example, no firm conclusions can be made as to the existence and the magnitude of an isotope effect for the chlorine isotopes. When $NaClO_3$ crystals are irradiated with neutrons, the retention of radioactive chlorine for the reaction $^{37}Cl(n,\gamma)^{38}Cl$ is, according to some[7,19], 1.5%, and according to others[30], 3.5%. For the reaction $^{35}Cl(n,\gamma)^{36}Cl$, studied by a third group of investigators[31,32], the retention rises to 12.5%. In the photonuclear reaction[52] $^{35}Cl(\gamma,n)^{34}Cl$ the retention in $NaClO_3$ is approximately 9%. Although the last result does not differ too drastically from the others, it is impossible to estimate the extent to which the picture is distorted by the effect of the high gamma background on the target crystals during the photonuclear reaction, *i.e.* by radiation-induced annealing. Further studies of the effect of X-rays and γ-rays on retention are needed.

The discrepancy is much more serious when the retention of radioactive chromium in sodium and potassium chromates is investigated by comparing results pertaining to a photonuclear reaction on the one hand and to a neutron capture reaction on the other. The reaction $^{50}Cr(n,\gamma)^{51}Cr$ gives a retention[27,28] of the order of 60–80%, but in the photonuclear reaction $^{50}Cr(\gamma,n)^{49}Cr$ the retention drops[53] to 0%. It is difficult to point to the causes of this difference. Experiments on the radiation-induced annealing of neutron-irradiated K_2CrO_4 crystals have shown that the retention of radio-chromium is increased by the action of γ-rays on the crystals. Thus, we can dismiss the gamma background as a possible cause of decreased retention, although experiments in which potassium chromate was irradiated with 1.8 MeV electrons prior to neutron irradiation revealed[54] a slight decrease in retention as compared with the control crystals. It is worth noting that the difference in retention between (n,γ) and (γ,n) reactions is much smaller[53] in dichromates.

From the Seitz–Koehler theory we can state that at high recoil energies (*e.g.* in photonuclear reactions) the retention is independent of the recoil energy and of the specific nature of the primary event of the nuclear reaction: in other words, an isotope effect is not expected. This conclusion stems from the postulate that, when energy is lost in a given crystal, a particular atom must dissipate a strictly constant amount of energy in the hot zone. This is a very important concept, since it offers an experimental criterion for distinguishing between the true isotope effect and the influence upon retention of the type of nuclear reaction employed and of the magnitude of the recoil energy dissipated in the hot zone.

5. Characteristics of Some Chemical Systems. Effect of Structural Defects on Retention

There are considerable difficulties in interpreting the chemical recoil processes taking place in compounds not in their highest oxidation state at the time of irradiation. Typical of such systems are the hexahalogenorhenites K_2ReCl_6 [50,51] and K_2ReBr_6,[55] in which the rhenium is in the Re^{IV} state. When these compounds are irradiated some of the rhenium recoil atoms take up a valency of 7, and are removed from the target crystals in the form of the anion ReO_4^-. Over 30% of Re^{VII} is formed when K_2ReCl_6 is irradiated.

These results could be explained by Libby's model[19] of the ionisation of the central complex-forming atom during recoil. This involves the assumption that the radicals $ReCl_5^-$, $ReCl_4$, $ReCl_3^+$, $ReCl_2^{2+}$, etc., are formed. On Libby's model, heptavalent rhenium should be formed by the reaction between the positively charged radicals and water, with formation of radicals in which the rhenium is converted into a still higher oxidation state rather than being reduced. This seems an unlikely explanation, and it is probably more correct to postulate oxidation of the tetravalent rhenium by the neutral chlorine, formed during the irradiation of the crystals.

Libby's hypothesis is equally unsuccessful in explaining how the higher oxidation states, formed during neutron irradiation, are removed by thermal annealing. Whereas the annealing process in chromates can be described as recombination of the radicals $CrO^{4+} + O^{2-} \rightarrow CrO_2^{2+}$, leading to increased concentration of Cr^{VI} in solution, such a recombination mechanism can hardly be applied, say, to irradiated sodium arsenite or As_2O_3.[56,57]

The initial distribution of valencies for a number of arsenic compounds is shown in Table 3.

Annealing of the last two compounds given in the table removes the pentavalent arsenic and stabilises the whole of the arsenic in its original trivalent state. If we assume that the primary recoil products in As_2O_3 or in $NaAsO_2$ are the radicals AsO_2^-, AsO^+, and As^{3+}, it becomes difficult to understand the formation of ~ 4% of As^V. Even less likely is the hypothetical annealing reaction written, by analogy with other systems,

$$As^{3+} + O^{2-} \rightarrow AsO^+,$$

which fails to explain the increased retention in the original trivalent state on heating. In As_2O_3, for example; oxygen exchange between As^V and As^{III} in the hot zone seems more likely:

$$As_2O_3 \rightleftarrows As_2O_5. \qquad (15)$$

The high retentions of radioactive chromium in solid solutions of potassium chromate and potassium sulphate[28] irradiated by thermal neutrons, and of radio-manganese (up to 50%) in similarly irradiated potassium permanganate–perchlorate mixed crystals[58], can be explained in terms of reactions in the hot zone between recoil fragments and molecular or atomic oxygen. According to Libby's hypothesis, oxygen atoms should be set free when S–O or Cl–O bonds are broken, whilst oxygen ions are expected from the rupture of Cr–O and Mn–O bonds. The recoil products in irradiated mixed crystals of this type will find themselves in a medium of relatively high oxidising power, tending to raise the yield of recoil atoms in the highest valency state. The high concentrations of pentavalent phosphorus (70–100%) in crystals of K_2SO_4, $KClO_4$, $KClO_3$,[59] K_2SO_4, Na_2SO_4,[60-62] $CaSO_4$,[63] Na_2SO_3, and $Na_2S_2O_3$,[61-62] irradiated with fast neutrons, may arise from processes of the same type. In salts not containing oxygen as one of the lattice components, *e.g.* NH_4Cl and KCNS, the concentration of P^V fell to 30%,[61,62] in accordance with the hypothesis which postulates oxidation of the hot atoms by oxygen in the thermal spike. Water of crystallisation favours, as a rule, the oxidation of radioactive traces in crystals.

Oxidation reactions in the hot zone are probably responsible also for the high yield (~ 100%) of Cr^{VI} in the positron decay of ^{51}Mn to ^{51}Cr in $CsMnO_4$ crystals[64]. The same argument can be applied to manganese carbonate crystals. The primary positron decay event produces a molecule-ion. A process of the type

$$MnCO_3 \xrightarrow{\beta^+} CrCO_3^-$$

justifies the expectation that the radio-chromium will appear in its lower valency states. Studies of the chemical forms of the radioactive chromium detected ~ 30% of Cr^{VI} among the manganese decay products. This relatively high yield of hexavalent chromium is due, according to Harbottle, to reactions between chromium recoil atoms and dislodged oxygen atoms or carbonate ions[36].

In alkali metal halide crystals the Szilard–Chalmers effect has some specific characteristics. Recoil atoms are usually obtained in these systems by nuclear reactions involving a change in atomic number of the target element, such as (n, p), (n, α), etc., and therefore the new elements find themselves in an electrostatic field, which is unusual for them. Various authors have investigated the chemical state of sulphur[65], phosphorus,[59,66-68] and arsenic[69] in different alkali metal halide crystals.

The recoil energy of sulphur and phosphorus atoms formed in alkali metal chlorides by the nuclear reactions $^{35}Cl(n, p)^{35}S$ and $^{35}Cl(n, \alpha)^{32}P$ amounts to 15 and 50 keV respectively. When a positive particle is ejected from a ^{36}Cl nucleus, the atom becomes negatively charged if all the outer-shell electrons are retained. We might expect S^{2-} and P^{3-} anions to appear in the lattice; however, since

TABLE 3. Retention in compounds of arsenic, irradiated with neutrons.

Compound	Irradiation temperature, °C	As^V, %	As^{III}, %	As^0, %	No. of experiments
As_2O_5	room	46.8	51.9	1.32	4
As_2O_5	—78°	40.8	57.8	1.43	4
$NaHAsO_4$	—78°	55.9	43.4	0.74	2
As_2O_3	—78°	4.17	94.8	1.067	6
Na_2AsO_2	—78	4.6	94.5	0.85	2

the first electron affinity of a neutral phosphorus atom is 0.8 eV, and that of a neutral sulphur atom is 2.4 eV, one or several of the outer electrons will be lost at the recoil energies in question, and the most probable state of the recoil atoms becomes one of the lower valency forms, such as P^0 and P^+ for phosphorus and S^- and S^0 for sulphur.

Indeed, experiments have shown that the sulphur in KCl crystals is predominantly in the form of the ions S^{2-}, S^-, or of elementary sulphur, and that the fast isotope exchange causes these forms to be indistinguishable[65]. Similarly, approximately 80% of the radio-phosphorus passes into the solution in the form of phosphine and hypophosphite. The pentavalent phosphorus or arsenic in carefully degassed alkali metal halide crystals usually amounts to ~10% of the total activity of these elements.[68,69] The lack of dependence of the yield on solvent pH is evidence that the valency states are stabilised in the crystal. On heating, the lower valencies are oxidised to the pentavalent state, which may be thought to involve $KPCl_6$ complexes. It is assumed that complexes of the type K_2PCl_6 and K_3PCl_6 are also present. The oxidising agents which operate during annealing are probably V-centres, produced by the radiation.

It has been repeatedly stated that the intermediate recoil products disproportionate in contact with water. Thus, the fact that annealing KCl crystals which have been irradiated with high-energy protons increases the radioactive fractions of both P^V and P^{III} is interpreted[68] as evidence for the existence of the species PCl_4 (tetrahedral configuration) in the crystals after irradiation, this species being equally likely to suffer oxidation or reduction by water when the crystal is dissolved. Carlson and Coski[67] separated the radio-phosphorus formed in KCl crystals by the $^{35}Cl(n, a)^{32}P$ reaction into the three valency states 3-, 3+, and 5+, and found that in some of the experiments the 3- and 3+ forms were present in roughly equal amounts. They concluded that the elemental phosphorus present in the lattice disproportionates, when in contact with water, into two valency states (3- and 3+) which are extracted by the phosphine and hypophosphite–phosphite carrier[67].

If the crystals are not heated to a high temperature before irradiation, so as to remove possible traces of occluded oxygen and water and to annihilate dislocations and other structural defects, most of the sulphur and phosphorus appears in the 6+ and 5+ valency states respectively. This is difficult to explain merely by the formation of the oxide chlorides $SOCl_4$ or $POCl_3$, because oxygen or water are very sparsely distributed in the lattice of "anhydrous" alkali metal halides, and a radioactive atom is very unlikely to penetrate to the immediate vicinity of one of these impurities, particularly since oxygen diffusion is quite negligible at room temperature. Obviously, the phenomenon must involve the migration of electron vacancies (positive holes) from the oxygen to the phosphorus and sulphur.

A similar mechanism must be responsible for the oxidation of radioactive impurities under the influence of ionising radiation: the radiation accompanying neutron interaction, γ-rays from ^{60}Co, or X-rays. Radiation leads to the formation of neutral chlorine in the KCl crystal lattice. Elemental phosphorus, formed by the nuclear reaction, interacts with neutral chlorine or with various V-centres by an electron–hole mechanism; this leads to the production of radicals of the type PCl, which undergo oxidation and reduction when the crystal is dissolved. At high doses of γ-rays the concentration of free chlorine increases, and these radicals are converted into PCl_3 and PCl_5 and ionic complexes including potassium ions of the lattice. In this way the amount of pentavalent phosphorus can rise[67] to 100%. Intense irradiation with γ-rays prior to the neutron reaction will, presumably, have a similar effect.

Since each recoil atom disturbs the perfect periodicity of the lattice field, and can act as an electron donor or an electron acceptor, even the mildest electronic processes in the lattice can be expected to affect the chemical state of such an extraneous atom.

Ordinary daylight, by dissociating F-centres and setting free electrons, should give a lower yield of the more oxidised forms. The presence of foreign impurities at concentrations several order of magnitude higher than those of the radioactive atoms can affect the stability of the colour centres and thus affect the chemical fate of the recoil atom. Impurities and defects will also influence the diffusion of oxidising agents during thermal annealing: this can affect the rate and the kinetic order of the annealing reaction. Unfortunately, only one publication (by Süe and Caillat[66]) deals with these aspects. The authors attempted to correlate the ratio of the valency states of radiophosphorus in the crystals after irradiation with the presence of radiation-induced lattice defects. They investigated the state of phosphorus in crystals of LiCl, NaCl, and KCl which had not been degassed before irradiation. In all three cases the amount of P^V was ~40–50%. Also, by heating a crystal of NaCl for a few minutes at 350°, they decreased the proportion of the pentavalent form from 43% to 31%. According to the authors, electrons bound in F-centres are freed by raising the temperature (which also bleaches the crystal), and are trapped by pentavalent phosphorus ions thereby lowering their valency.

It follows from what has been said in this section that one can only speak of the ratio of oxidised and reduced forms in the context of strictly constant irradiation and other conditions (pretreatment and subsequent storage) of the crystals.

Evidently, systems including an oxy-anion such as chromate are more stable towards various adventitious interactions. It has been reported[27] that retention in chromates is unaffected by four hours' illumination in bright sunlight. But even in these crystals the behaviour of recoil fragments depend on structural defects or inactive dislocations[54,70]. For example, whereas for monocrystalline chromates the retention was 77.3%, it was found to be 69.9% for microcrystalline powders. Retention in chromates and in bromates is decreased also by previous irradiation with electrons of 1.8 MeV energy. The variation of initial retention in $Ca(BrO_3)_2$ with dose of electron radiation prior to neutron irradiation is shown in Fig. 4.

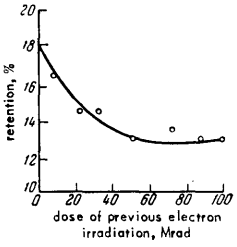

Fig.4. Influence of previous electron irradiation (energy 1.8 MeV) on retention in $Ca(BrO_3)_2$.

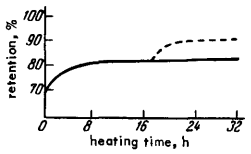

Fig.5. Effect of comminution of the crystals in the course of isothermal annealing on retention in potassium chromate. Full line — annealing of single crystal; broken line — annealing of specimen ground to a powder at a predetermined stage.

TABLE 4. Effect of temperature of neutron irradiation on retention in $KMnO_4$.

Irradiation		Storage		Dissolution			Retention, %
T, °C	time	T, °C	time	T, °C	time, min	medium	
90–190*	150 min	room	30 min	room	–	H_2O	38.8
30	15 s	+25	2 h	+2	5	H_2O	20.7
30	15 s	+25	2 h	−60	10	acetone	19.3
30	15 s	−78	2 h	−60	10	acetone	15.6
−78	15 s	−78	2 h	+21	5	acetone	18.2
−78	15 s	−78	2 h	−60	10	acetone	8.9
−195	90 min	−195	1 h	−90	15	acetone	5.1

* Value at 90–190° taken from Sano [74].

It is obvious that ionic vacancies in the crystal lattice can facilitate the diffusion of recoil fragments when the crystals are heated, and therefore also increase the rate of thermal annealing. Andersen and Maddock [71] have shown that, when small amounts of calcium are added to potassium chromate in order to introduce cation vacancies, the radioactive chromium is annealed appreciably faster, whereas the initial retention value is practically indistinguishable from that for the pure crystals.

The influence of structural defects on the rate of chemical reactions during heat-treatment can also be demonstrated in the following way. A crystal, annealed at a given temperature until it reaches its plateau, is exposed to strong ionising radiation, and annealed once again at the same temperature. Under these conditions the retention shows a rapid rise to a new plateau. Exactly the same behaviour is observed, at least qualitatively, if the exposure to radiation is replaced by comminution and grinding of the single crystals at a given stage of annealing. The full line in Fig. 5 shows the retention in K_2CrO_4 crystals as a function of annealing time at 230°; the broken line shows the retention of a portion of the same material which was powdered after 16 hours' heating [71].

6. Variation of Retention with Crystal Irradiation Temperature

Data on the thermal annealing of irradiated crystals indicate that, as a rule, retention is increased by annealing. It seems reasonable to suppose that the temperature of neutron irradiation must have a similar effect: higher irradiation temperatures should produce increased retention, and *vice-versa*. Such is in fact found to be the case in all systems investigated up to now: potassium chromate [28], bromate [72], hexachlororhenite [51], and permanganate [73]. Harbottle's results for the retention in potassium permanganate [73] irradiated at different temperatures are reproduced in Table 4 as an example of this temperature effect.

The uniqueness and the superiority of Harbottle's experiments (as compared with those of other workers) lie in his use of acetone at temperatures well below 0° to dissolve his crystals after irradiation. This enabled him to avoid to some extent recombination of the thermally unstable radioactive fragments present in the crystal, and to arrive at a retention value close to the true initial value and free from errors due to thermal annealing during irradiation at room temperature. Inspection of Table 4 suggests that the highest retention value in the absence of bond breaking in the oxy-anion is less than 5%, and that at least 3/4 of the retention observed at room temperature results from annealing, which occurs at an appreciable rate even in the temperature range from -60° to -90°. (It is quite possible that the higher retention of $KMnO_4$ as compared with other alkali metal permanganates is due to easier annealing of the manganese recoil atoms in $KMnO_4$ even at room temperature.)

It must be noted that one worker [74] has reported an increase in $KMnO_4$ retention with decreasing temperature in his low-temperature investigation of $KMnO_4$. There appears to be a minimum at about 0° in the plot of irradiation temperature against retention. These experiments involved dissolution of the crystals in water, which raises some doubts as to the reliability of the results. Clearly, an explanation of the discrepancy between these data and those of Harbottle must be sought in the processes occurring when the crystals are dissolved in water. These processes may be quite different for crystals which have been subjected to high-temperature and to low-temperature irradiation.

The irradiation temperature has a specially strong effect on the formation of different chemical forms of phosphorus during neutron irradiation of phosphates [75-78]. The phenomena reflect the specific tendency of phosphorus atoms towards polymerisation, and the complicated chemistry of the oxy-anions of phosphorus. For example, when Na_2HPO_4 is irradiated at dry-ice temperatures, ~ 80% of the radioactive phosphorus appears in the pentavalent state, although the P^V fraction has a very mixed composition. On the other hand, only a single radioactive phosphate is formed, effectively, at irradiation temperatures of 30–50°. This may be due to the extreme instability of the recoil fragments and their high sensitivity towards annealing reactions even at these temperatures. Another possible cause is too low a recoil energy of the phosphorus atom, such that this atom cannot tear itself from the very stable and compact PO_4^{3-} unit. It would be difficult to explain otherwise why the phosphorus atoms ejected from the oxy-anion produce exclusively phosphate rather than some other phosphorus compound. This argument, plausible at the moment, will become convincing if complex compounds such as pyrophosphate and trihypophosphate are irradiated, and the whole of the radioactivity is found in the form of the parent compound.

We cannot, unfortunately, draw definite conclusions about the mechanism of these processes, because our knowledge of the stability of phosphorus radicals and of their reactivity in the solid phase is quite inadequate, as is also our understanding of the γ-ray spectrum of the

reaction $^{31}P(n,\gamma)^{32}P$. Furthermore, different workers have applied different analytical procedures in these investigations.

7. Effect of Solvent pH and of Analytical Method upon Retention

In studies of recoil processes it is very important to allow for the presence of every possible radical and intermediate valency compound in the crystal after irradiation, whose reactions with water may depend on the pH of the solution. One must also bear in mind the possibility of various physicochemical processes during dissolution, which may also be sensitive to pH.

For example, the retention of permanganates increases from 10–20% when the crystals are dissolved in a neutral medium to 100% in alkali [19]. Libby explains this by postulating that heptavalent manganese radicals are reduced by water in acid and in neutral media, but are hydrolysed in alkaline media, thus:

$$4MnO_3^+ + 2H_2O = 4MnO_2 + 3O_2 + 4H^+,$$

$$MnO_3^+ + OH^- = MnO_4^- + H^+.$$

More recent work [29] has shown that this increased retention can be ascribed to adsorption of radioactive manganese on colloidal particles of inactive MnO_2 in alkaline solution, followed by heterogeneous manganese exchange (these colloidal particles are always present in permanganate to some extent). High retention in acid solutions can probably also be explained by some form of exchange, *e.g.*

$$Mn^*O_3^+ + MnO_4^- \rightarrow MnO_3^+ + Mn^*O_4^-. \qquad (16)$$

A sharp change in retention with increase in pH has been observed also in potassium chromate, if the activity is isolated in the form of chromium hydroxide [27]. There are reasons for ascribing increased retention in this case to the formation of salts of the type $Cr(OH)CrO_4$.

Table 5 shows the complicated effect [69] of solution acidity on the yield of pentavalent arsenic from irradiated crystals of the hydrate $LiBr.H_2O$.

Neither anhydrous LiBr nor the dihydrate show this dependence. Hence this behaviour of the monohydrate must be thought to result from the presence of some intermediate species in the crystal after irradiation, the reaction between water and this species being a complicated function of pH. In anhydrous LiBr or in the dihydrate this form is absent, or is present in very low concentrations. Studies of the effect of solution pH on other crystals may provide some information on the chemical forms in which the recoil atom is stabilised within the crystals.

TABLE 5. Effect of pH of solvent medium on the yield of pentavalent arsenic in $LiBr.H_2O$.

pH	As^V, %
0.5	51 ± 1
2.5— 2.8	55 ± 1
9.2— 9.6	57 ± 2
10.5—10.9	68 ± 1
10.7—11.2	72 ± 2
10.9—11.2	73 ± 2
11.1—11.6	60 ± 2
11.2—12.0	53 ± 2
12.0—13.0	54 ± 2

At the beginning of this article brief mention was made of the different methods of investigating the chemical processes accompanying recoil, and it was pointed out that the carrier method followed by precipitation of the chemical form of interest, which is most widely used, does not reflect all the complications of the problem. The retention values obtained by this method result from the combination of several unknown fractions, coprecipitated with the parent form. Hence the results usually contain a systematic positive error as compared with the true initial retention. This effect is illustrated in Table 6, which gives the retention values for hexachloroiridates obtained by electrophoresis and by caesium precipitation respectively [49,79].

Only the values obtained by precipitation can be fitted satisfactorily on a plot of retention against the standard oxidation potentials of the systems, taking the potential of the system $[Ir(III)Cl_6]^{3-}/[Ir(IV)Cl_6]^{2-}$ as 0.93 V. Thus the results obtained by electrophoresis are not compatible with the retention values obtained for other systems by precipitation.

A similar state of affairs is observed with bromates. The electrophoretic results give retention values of 9–13%, showing some correlation with the nature of the cation [33]. A less accurate extraction method gave a retention of 18–22% for all cations. [70,72,80] This type of discrepancy also makes it impossible to draw definite conclusions from studies of Szilard–Chalmers processes in phosphates, as stated in the previous section.

Hence, the need for the greatest care in the choice of analytical procedure and in the interpretation of results cannot be overemphasised.

8. Possible Applications of the Mössbauer Effect in Hot Atom Chemistry

We have seen that, when an atom produced by a nuclear reaction or by a radioactive transmutation becomes part of the composition of a solid crystal, one has to resort to precipitation and separation of the products of the reaction between hot atoms and the surrounding medium. Unstable intermediates are, of course, lost in the process, and we cannot be certain that the spectrum of products obtained in this way is independent of the chosen analytical procedure. In this context it is relevant to mention the new opportunities offered to chemists by the Mössbauer method (recoilless resonance absorption of the gamma-quanta emitted by a radioactive nucleus).

The principle of the so-called Mössbauer effect lies in the ability of unexcited nuclei to absorb, by resonance, the gamma-quanta emitted by the transition of an excited

TABLE 6.

Compound	Retention, %	
	electrophoresis	precipitation
$NaIrCl_6 \cdot 6H_2O$	6.7 ± 2,0	67.9 ± 0.8
$(NH_4)_2IrCl_6$	14.1 ± 0.5	59.9 ± 0.2
K_2IrCl_6	25.5 ± 1.2	99.3 ± 0.1

nucleus to the ground state. The unexcited nucleus is thereby promoted to an excited state. A similar phenomenon is well known in conventional optics: the only difference is that the relatively large momentum of γ-quanta should impart a strong recoil to both the emitting and the absorbing nucleus, and thus make resonance absorption impossible because of the Doppler effect. Mössbauer showed, however, that at least in some cases the recoil is taken up by the crystal (or heavy molecule) as a rigid whole, so that recoil phenomena can be neglected.

The Mössbauer effect observed in iron is a good example. The source of radiation was iron (stainless steel) whose surface had been alloyed with radioactive cobalt (^{57}Co, $T_{1/2}$ = 270 days). The ^{57}Co undergoes electron capture, and is converted into ^{57}Fe in an excited isomeric state ($T_{1/2} = 10^{-7}$ s). The gamma-quanta emitted during the isomeric transition, of energy 14.4 keV, can be absorbed by resonance in ordinary iron, or, better, in iron enriched with ^{57}Fe‡.

To observe the Mössbauer effect, the absorber is set into uniform translational motion with respect to the source, and the transmission is measured as a function of the relative velocity. If absorber and source are physically and chemically identical, an absorption maximum is observed at $v = 0$. A different state of affairs obtains when the identity between absorber and emitter is destroyed. This is because the probability density of finding s electrons from the atomic shell within the volume of the nucleus is non-zero. Due to coulombic interaction, this causes a displacement of the energy levels of the nucleus, thus affecting the energy of γ-quanta emitted or resonantly absorbed (the so-called isomer shift). In different chemical compounds of a given element the density of s electrons in the nucleus is different, and therefore the values of the isomer shifts are also different.

On the other hand, the interaction between the nuclear moments and the moments of the electron shells causes hyperfine splitting of the nuclear energy levels. The nature and magnitude of this splitting are determined by the electron density distribution in the compound to which the atom belongs.

The high sensitivity of the Mössbauer effect to extremely small ($\sim 10^{-8}$ eV) changes in the energy of resonance absorption of γ-quanta sometimes makes it possible to identify the type of chemical binding of an atom, whether emitted or absorbed, from the Mössbauer spectrum.

Up to now, the compound under study has mostly been used as the absorber. However, if ^{57}Co is introduced into the molecule (or crystal) of the emitter, the energy of the gamma-quanta emitted after radioactive conversion of this isotope into ^{57m}Fe will correspond to the chemical forms produced immediately following the radioactive disintegration of the ^{57}Co by the primary interaction between the hot ^{57m}Fe atoms and the medium. Under these conditions one observes the spectra of the ^{57m}Fe atoms in exactly the states which have been produced in a time of the order of 10^{-7} s (the lifetime of the isomer state).

Experiments of this type have been made by Wertheim[81], who studied the valency states of iron produced after decay of ^{57}Co in CoO.

It should be noted that the capture of an orbital electron by a nucleus lowers the charge on the nucleus and on its electronic environment by one unit. Thus we can expect the daughter atom to have the same valency as the parent atom. But this can only happen if the atom excited after electron capture, such as ^{57m}Fe, passes into its normal state exclusively by X-ray emission. If the excitation of the atom is "relieved" by a single-stage Auger process, the iron atom appears in the Fe^{3+} state. Two-stage ionisation by this same process will lead to Fe^{4+} ions, and so on. We can assume that the electron affinity of multiply charged atoms is so large that their lifetime in the crystal works out at appreciably less than 10^{-7} s, and they cannot be detected by the Mössbauer effect.

Fig. 6 shows a Mössbauer spectrum taken at 169°K. It consists of two series of emission bands. These series, which combine two hyperfine splitting structures, differ in line intensity and line width. Such a composite picture of two series can arise either from quadrupole splitting or from the presence of two non-equivalent types of iron, distinguishable by their position in the lattice or by their valency state. The quadrupole splitting explanation can be rejected, since the intensities of the two series are very different, and this would be surprising since CoO has an almost cubic symmetry. The assumption that the ^{57m}Fe atoms occupy positions different from those of the normal cobalt atoms is untenable, since the recoil due to the neutrino associated with the electron capture process is hardly likely to displace an atom from its lattice site. The only remaining explanation is that the difference between the iron atoms concerns their state of charge, and that the two most stable valency forms of iron, Fe^{2+} and Fe^{3+}, are involved. Comparison of the isomer shifts with those observed in compounds of divalent and trivalent iron confirms this assumption.

It is clear from Fig. 6 that the emission lines are wider for Fe^{3+} than for Fe^{2+}. The line widths for divalent iron do not differ significantly from normal line widths; the greater line width for trivalent iron can arise either from differences in the immediate surroundings of the trivalent atom or from the fact that the charge of +3 is unstable, and disappears in a time not much greater than 10^{-7} s.

Differences in the immediate surroundings can arise as follows: a higher valency state, such as Fe^{4+}, disappears by capturing an electron from the surrounding divalent cobalt atoms and forming a trivalent iron atom with a Co^{3+} nearest neighbouring. In this way, local environments can be generated whose field at the trivalent iron nucleus is somewhat different. This process should be capable of reducing all the highest charged states to Fe^{3+} in a time comparable with 10^{-7} s. Whether or not trivalent iron

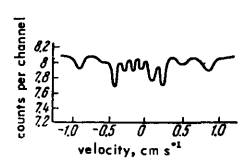

Fig. 6. Hyperfine structure of γ-transitions of 14.4 keV energy in divalent and trivalent ^{57m}Fe in cobalt oxide at 169°K (Mössbauer emission spectrum). The central part of the spectrum, consisting of narrow lines due to Fe^{2+}, can be readily distinguished.

‡ The concentration of ^{57}Fe in ordinary iron is 2.17%.

itself is stable is a question which can be partly solved by examining the relative intensities of the Fe^{2+} and Fe^{3+} emission bands. From the fluorescence yield it appears that approximately 1/3 of the disintegrations gives divalent iron, but the ratio of intensities observed is significantly higher. We may conclude, therefore, that trivalent iron is partly converted into divalent iron in a time of somewhat more than 10^{-7} s. This electron exchange process between Fe^{3+} and Co^{2+} can be quite favourable energetically.

The second paper which we shall discuss was published recently by de Coster and Amelinckx[82]. The authors introduced $^{57}CoCl_2$ into single crystals of KCl by diffusion, and studied the state of the iron formed in the potassium chloride after radioactive disintegration of the cobalt. Different results were obtained for mixed crystals of this type whose previous thermal histories were different. The Mössbauer absorption spectrum for crystals slowly cooled to room temperature from a few hundred degrees consists of a single peak, whose appearance suggests the absence of quadrupole splitting, due no doubt to the cubic symmetry of the surroundings of the cobalt atom in the $CoCl_2$ diffusion layer. The position of the peak, however, and the magnitude of the isomer shift, imply that the rays are emitted from iron in the Fe^{3+} state.

A different picture is obtained if the mixed crystals are rapidly cooled over the same temperature interval. The peak splits into two components of approximately the same height, the width of the composite peak being greater than for the slowly cooled specimen. This can be due to quadrupole splitting. The authors ascribe the effect to a large number of vacancies being "frozen" in the crystal after rapid cooling. These vacancies have a tendency to associate with impurity ions of opposite valency due to coulombic interaction. The cobalt ions attract cation vacancies, which carry an effective negative charge and are relatively mobile at room temperature in KCl. The formation of a (cobalt ion + vacancy) complex perturbs the cubic symmetry of the surroundings of the cobalt ion, and thus induces quadrupole splitting. The trivalent iron therefore appears, in this system, bound to a cation vacancy of the potassium chloride crystal lattice.

As we have seen, the Mössbauer effect offers valuable information on the chemical consequences of various nuclear transformations. It is becoming increasingly more important, owing to the growing number of suitable radioactive isotopes and of experimenters who are prepared to master the technique.

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COMMERCIAL METHODS OF SYNTHESIS OF α,β-UNSATURATED ALDEHYDES AND KETONES

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I. INTRODUCTION

α,β-Unsaturated aldehydes of the acrolein series and ketones are of great interest as starting materials for the production of polymers and copolymers with an active functional (carbonyl) group; they can also be used to obtain other monomers and many other products.

Acrolein has already become an important commercial material. Industrial methods have been developed for the production from it of allyl alcohol[1-4], glycerol[5-7] and its derivatives[8], and acrylonitrile[9-11]. The chemistry of acrolein has recently been attracting great attention[12-20]. In the Federal Republic of Germany intense work is going on on the polymerisation products of acrolein itself[21,22]. Furthermore, even now a considerable quantity of acrolein is used for the production of methionine, a substance which accelerates the growth of poultry when added to their feed[23]. In the U. S. A. the Carbide Chemical Corporation has constructed a plant for the production of a number of acrolein derivatives on an industrial scale[24,25].

Methacrolein has not yet found wide use as a commercial intermediate because it is much less readily available, but potentially it is of interest for chemical synthesis. According to the literature[26-30] methacrolein is readily converted into substances of value to the plastics industry, such as methacrylic acid, methylallyl alcohol, and polyhydric alcohols.

α,β-Unsaturated ketones have also not yet taken on great industrial significance, apparently mainly because of their relatively low availability. There are reports[31] of the preparation from polyvinylketones of lacquers, unbreakable glass, plastics, and so on. Colourless monomers produce crystally pure polymers of remarkable optical properties[32]. Many copolymers of methyl vinyl ketone[33-35], isopropenyl methyl ketone[36-44], and phenyl vinyl ketone[45,46] have been described. There are indications[47] that after treatment with phosphoric acid copolymers of styrene with methyl vinyl ketone or isopropenyl methyl ketone are extremely resistant to heat and withstand the action of a

flame. Rubbers prepared by the emulsion copolymerisation of isopropenyl methyl ketone with divinyl are better than divinylstyrene rubbers in some of their properties[48].

II. SYNTHESES OF α,β-UNSATURATED ALDEHYDES OF THE ACROLEIN SERIES

There were no commercially acceptable methods for the production of acrolein until the 1940's, when the German firm of Degussa developed an industrial method for its production by the aldol condensation of formaldehyde with acetaldehyde[49].

In the United States in 1946–1948 the Shell Chemical Corporation developed a commercial method for the synthesis of acrolein by the pyrolysis of diallyl ether[50], which is a by-product in the preparation of allyl alcohol from allyl chloride[51]. Acrolein has been obtained by this method in a plant of capacity ~9 tons per month[50]. The pyrolysis is carried out at 520° and 2.1 atm.; the yield of acrolein based on reacted ether was 86% at a conversion of ether of 90% per pass. This method has no commercial significance at present, because it is more economical to prepare allyl alcohol from acrolein.

The possibilities of the industrial utilisation of acrolein increased significantly when acrolein was shown to be obtainable in high yield by the oxidation of propene. At present this is considered the most promising method for the synthesis of acrolein.

Methods for the production of methacrolein have also been improved. A patent[52] describes the production of methacrolein in 57–60% yield by the pyrolysis at 500–570° of di-2-methylallyl ether, which is a by-product in the preparation of methylallyl alcohol by the alkaline hydrolysis of 3-chloro-2-methylprop-1-ene.[53]

Methods are now being developed for the production of methacrolein by the aldol condensation of formaldehyde with propionaldehyde and by the oxidation of isobutene.

The preparation of methacrolein and other α-alkylacroleins by the Mannich reaction has recently been shown to be commercially feasible.

At present there are thus several convenient methods for the production of α,β-unsaturated aldehydes of the acrolein series. Depending on the actual circumstances, the following are commercially feasible: the oxidation of alkenes, the aldol condensation, and the method based on the Mannich reaction, and these are considered in more detail below.

1. Production of α,β-Unsaturated Aldehydes by the Direct Oxidation of Alkenes

As already stated, the direct oxidation of propene is considered abroad as the most promising method for the production of acrolein:

$$CH_2=CH-CH_3+O_2 \xrightarrow{200-450^\circ} CH_2=CH-CHO+H_2O.$$

Similarly isobutene can be oxidised to methacrolein:

$$CH_2=\overset{CH_3}{\overset{|}{C}}-CH_3+O_2 \longrightarrow CH_2=\overset{CH_3}{\overset{|}{C}}-CHO+H_2O.$$

In 1950 the Shell Chemical Corporation set up a test plant for the catalytic oxidation of propene to acrolein of capacity 2 tons per month[54], and at the end of 1959 it opened a factory for the production of glycerol from acrolein; this is still the largest works in the world for the production of acrolein, its annual capacity being estimated at 13 620 tons of acrolein[22]. A similar process has been developed and taken to the pilot plant stage by the Italian firm of Montecatini[55-58].

The literature on this method is mainly concentrated in patents, and only in recent years have these processes attracted any considerable attention from Soviet chemists, who have published a good deal of work on the choice of catalysts and the influence of various factors on the process[59-91].

The reaction is conducted at 200–450° and pressure close to atmospheric[22,92-94]. The propene : oxygen ratio varies, according to different sources, from 2 : 1 to 30 : 1, the lower ratios being most often used. Air or a mixture of oxygen with carbon dioxide or steam is employed as oxidant. Paraffinic hydrocarbons are inert under these conditions and do not interfere in the process[95]; some patents even recommend their use as diluents[96].

Several types of catalyst have been described for the oxidation of alkenes: copper(I) oxide on a carrier[22]; copper(II) oxide on a carrier in the presence of selenium[22]; mixtures of various metals of variable valency or their oxides[97-105]; metal selenites or tellurites promoted by various oxides[106-108]; and molybdates, chromates, sulphates, molybdophosphates, vanadates, aluminates, and silicates of various metals (copper, bismuth, cobalt, and others)[59,109-114]. Copper(I) oxide is the most used[22].

As carriers there are used silicon carbide[22], ceramically combined compositions of aluminium and silicon[115], pumice[64], alumina[22], and others. The process can be successfully worked on a catalyst without any special carrier[57,58].

The main side reaction in the oxidation of propene to acrolein is the formation of carbon dioxide and water; considerable amounts of formaldehyde and acetaldehyde are also produced, as well as carbon monoxide, organic acids, various carbonyl compounds, and relatively small amounts of polymers, which can deactivate the catalyst.

The catalyst requires periodic regeneration. The reduced activity is manifested in two ways, a lessened selectivity and a lessened productivity, the former because of change in the composition of the catalyst, and the latter because of deactivation of the active centres by catalytic poisons or polymers[22]. Regeneration is therefore carried out in two ways: by changing the working conditions (reactant ratios and temperatures), which changes the chemical composition of the catalyst[116,117], and by burning off the deposits at a higher temperature (400–500°).[118]

Considerably improved yields of the unsaturated aldehydes are obtained by using halogens as promoters, added as such or as organic halogen compounds. Addition of 0.02 vol. % halogen derivative to the total reactant gas mixture increases the selectivity by 5–10% and the productivity of the catalyst by 30%.[87] Addition of iodine[119-121] has substantially increased the life of the catalyst, and has given a conversion of propene of 78–82% per pass with a 70–79% yield of acrolein. Without the halogen a greater selectivity requires a lower conversion per pass; according to the data available, the conversion of propene per pass should not then exceed 10–25%.[92-94]

Addition of selenium to copper catalysts considerably increases the selectivity and productivity of the catalyst.

According to Kruzhalov *et al.*[85], the selenium acts by blocking, by chemisorption, the active centres which catalyse the complete oxidation of the propene, while in the formation of acrolein it participates in the transfer of oxygen to the propene molecule. When using selenium the yield of acrolein reaches 81–82% with a propene conversion of 90–95% per pass. The recommended selenium concentration is 0.008–0.12 mg per litre of gas mixture[122]. Thus by using selenium the alkene need not be recycled, but because of its high toxicity it must be almost completely removed from the reaction gases, for example, by passing them through active carbon[123]. In recent years sulphur has been recommended instead of selenium, since this also increases the activity and life of the catalyst, but is not toxic[124].

As already stated, under analogous conditions isobutylene is oxidised to methacrolein; yields of 73–78% with an isobutene conversion of up to 33% are attained[84,124-133].

The oxidation of alkenes gives a complex mixture of products, and the separation of the reaction products and isolation of the pure unsaturated aldehydes is one of the main problems in the commercial operation of the process, and special methods have to be employed. Many patents have been devoted to this problem; the most important are referred to in Sherwood's reviews[22,92-94].

The production of unsaturated aldehydes by the oxidation of alkenes is very promising for large-scale production, since a cheap starting material is used. A substantial disadvantage of this method is the considerable technological difficulties involved in the industrial working of the process, especially in the separation of the reaction products.

2. Production of α,β-Unsaturated Aldehydes by the Aldol Condensation of Formaldehyde with Aliphatic Aldehydes

In 1950 Schulz and Wagner published the results of their investigations[49], which led to the development of the first industrial synthesis of acrolein by the aldol condensation of formaldehyde with acetaldehyde. In Germany in 1940 this method was taken to the pilot plant stage with a capacity of 1 ton of acrolein per month[49], and now there is a semi-industrial plant with a capacity of 10–20 tons per month[134]. Acrolein has been obtained by this method in the United States since 1955 by the Carbide and Carbon Chemical Corportion[135].

The reaction takes the course:

$$HCHO+CH_3CHO \rightarrow CH_2OHCH_2CHO \rightarrow CH_2{=}CH{-}CHO+H_2O.$$

In Germany the process is carried out in the vapour phase at 280–330° over silica gel of large pore size containing 10% sodium silicate[134], the latter reducing the formation of resins. Pure silica gel is extremely active, but even after 1 h its activity is completely lost because of almost complete resinification. When impregnated with sodium silicate the catalyst works for 150 h without marked diminution of activity, after which it can be regenerated by oxidation of 500–550° in a stream of water vapour and air.

Catalysts which have been recommended are magnesium silicate, calcium phosphate, aluminium phosphate, and alumina[49], also oxides of zinc, thorium, and titanium[136], and lead acetates and chromates[137].

At 300–325° and a contact time of 7–8 s, the yield of acrolein, based on reacted material, is 72–75% on the formaldehyde and 79–82% on the acetaldehyde (after losses during the separation) with an average conversion per pass of 50–52% for formaldehyde and 44–46% for acetaldehyde[49].

By-products of the reaction are crotonaldehyde (up to 10%), methyl formate (up to 3%), methanol (~6%), formic acid (3%), and small amounts of a gas consisting of CO, CO_2, and alkenes.

The yields obtained by the German workers have been confirmed by Dabagov *et al.*[138] Broad studies of this synthesis of acrolein have been conducted by Malinowski and coworkers[139-145], and it has attracted considerable attention in Japan[146-148].

The reaction products are separated by a relatively simple industrial rectification process[135]. An azeotropic mixture of acrolein and water (2.7–3.0% water) is obtained; when treated with 0.1% hydroquinone or other inhibitor it can be stored for several years.

The production of methacrolein by the aldol condensation of formaldehyde with propionaldehyde can be carried out in the vapour or liquid phase. The vapour-phase process is analogous to that for acrolein, and the same catalysts and reaction conditions can be used[137,149-151]. Thus one of the patents[151] indicates that methacrolein can be obtained in almost quantitative yield by carrying out the condensation at 300–320° over a catalyst comprising activated silica gel of large pore size impregnated with alkali metal phosphates or silicates. However, according to Malinowski[141-149] the yields of methacrolein in the vapour-phase condensation do not exceed 40–59%.

The liquid-phase process also uses various catalysts. Methacrolein has been obtained in 84.5% yield by carrying out the condensation at 100° in the presence of $BF_3.H_2O$;[125,152] the conversion of propionaldehyde was 24.9%. A patent[153] describes the production of methacrolein in high yield at 20–30° in the presence of sodium carbonate.

The aldol condensation of formaldehyde with other aldehydes having at least two hydrogen atoms on the carbon atom in the alpha position to the carbonyl group gives higher α-alkylacroleins in yields of up to 59%.[141,149,151]

The production of α,β-unsaturated aldehydes by the aldol condensation of formaldehyde with aliphatic aldehydes therefore has a definite technological value because it is simpler to realise industrially than the oxidation process, although it uses more costly starting materials.

3. Production of α,β-Unsaturated Aldehydes by the Mannich Reaction between Formaldehyde and Aldehydes

The wide possibilities in the choice of reagents, diversity of choice for the subsequent conversion of the Mannich bases, and the mild reaction conditions of the Mannich reaction have made it an important process in modern organic chemistry[154,155].

Investigators of the Mannich reaction were able to show a relatively long time ago that it can provide unsaturated compounds, including carbonyl monomers. However, for a long time this reaction had no technological value, apparently mainly because of its poor reproducibility. Mannich *et al.*[156] were the first to show the possibility of obtaining α,β-unsaturated aldehydes by this route.

This process (for example, for the production of methacrolein) is based on the reactions:

$$CH_3CH_2CHO+CH_2O+R_2NH\cdot HCl \longrightarrow \underset{\underset{CH_2NR_2\cdot HCl}{|}}{CH_3CHCHO} + H_2O,$$

hydrochloride of Mannich base

$$CH_3CHCHO \longrightarrow CH_2=\underset{|}{C}(CH_3)-CHO+R_2NH\cdot HCl.$$

(CH$_2$NR$_2$·HCl)

For the production of unsaturated carbonyl compounds the Mannich reaction is best carried out with salts of secondary amines. The use of ammonia or primary amines always leads to undesirable reactions, since the resulting Mannich bases, being primary or secondary amines, can themselves produce various by-products [157-159].

Beginning in 1939, a series of patents [160-164] and communications [165-167] appeared on the production of α,β-unsaturated aldehydes by this method. A main disadvantage of the method, which hindered its wide application, was that the yields of the unsaturated aldehydes varied, according to the data obtained by various workers, over very wide limits [160,161,163,164,166,167], with reaction times of from 6 to 24 h. [165,166] As a rule these syntheses had been carried out under conditions far removed from optimum, and had not been investigated from the point of view of the conditions necessary to ensure a high yield of the desired products.

The detailed investigations of Farberov and his coworkers [168-173] have enabled the irreproducibility of the Mannich reaction to be circumvented and have allowed the process to be taken to the stage of industrial realisation. As exemplified in the production of methacrolein, the rate of the Mannich reaction with aliphatic aldehydes was shown to be very strongly dependent on the pH of the medium. At pH 3-4, which is the usual range when the reagents are mixed in equimolar proportions, the reaction proceeds at a satisfactory rate only 100-120°, where there is a considerable polymerisation of the resulting unsaturated aldehyde. Adjusting the pH to 6-7 greatly accelerates the reaction and enables it to be conducted at relatively moderate temperature, and a nearly quantitative yield can be obtained. At pH 7 and 45° quantitative conversion is attained in 20-30 min. Heating the reaction products (without preliminary separation of the Mannich base) gives quantitative separation of methacrolein as an azeotrope with water. Pure methacrolein is readily obtained by azeotropic drying. The resulting amine salt solution can be recycled to the process after concentration. The synthesis of methacrolein (yield 98.7% of theory), α-ethylacrolein (97.9%), and α-isopropylacrolein (90%) is described. The methacrolein synthesis has been tested on a semi-industrial plant; a continuous process for its production has been developed in principle.

It is thus seen that the Mannich reaction can be used to obtain α,β-unsaturated aldehydes in yields close to theoretical, under very mild conditions and in very simple apparatus. The process requires more costly starting materials than the alkene oxidation process, but the practically quantitative conversion of the initial aldehydes per pass, the quantitative yields of α,β-unsaturated aldehydes, and the extremely simple apparatus, together with the complete absence of side reactions, make this process very profitable.

Another advantage of this method is the possibility of preparing a whole series of α,β-unsaturated aldehydes. The preparation of the following has been described: methacrolein [160-164,166,167], α-ethylacrolein [160-163,166,167], α-isopropylacrolein [165-167], α-propylacrolein [166,167], α-butylacrolein [166,167], α-t-butylacrolein [166], α-pentylacrolein [165], and α-phenylacrolein [162].

Recently Farberov and coworkers [174] have shown that this method can provide the previously unobtainable 2,4-dienals in high yields, so broadening the range of application of the Mannich reaction for the production of unsaturated aldehydes.

III. SYNTHESES OF α,β-UNSATURATED KETONES

α,β-Unsaturated ketones have long attracted the attention of investigators. Berlin's review of the methods of production of vinyl ketones [175] appeared as early as 1939. At present there are several commercially valuable methods for the production of α,β-unsaturated ketones.

1. Production of α,β-Unsaturated Ketones by Hydration of Vinylacetylenes

This method is of commercial interest mainly for the synthesis of methyl vinyl ketone.

The hydration of vinylacetylene to methyl vinyl ketone was first achieved by Nieuwland [176,177] and was subsequently studied in detail by Churbakov and Ryazantsev [178,179].

$$CH_2=CH-C\equiv CH+H_2O \rightarrow CH_2=CH-COCH_3.$$

The hydration is carried out in an acid medium in the presence of mercury salts (generally the sulphate) at a temperature not above 70-80°. [178,179] To prevent reduction of the mercury(II) to inactive mercury(I) an oxidising agent, such as iron(III) sulphate, is added to the reaction mixture to convert the mercury(I) salt into the active mercury(II) salt [178]. The yield of methyl vinyl ketone reaches 90% on reacted and 77% on taken vinylacetylene [178-180]. The patent literature describes apparatus for the continuous production of methyl vinyl ketone by this method [180-182]. Some patents recommend complete hydration of the vinylacetylene to acetoin in the presence of mercury(II) sulphate, with subsequent dehydration to methyl vinyl ketone [183,184]. The main disadvantage of this method is the use of toxic mercury compounds.

A relatively recent communication [185,186] reported the hydration of vinylacetylene in the vapour phase over catalysts not containing mercury: cadmium tungstate, cadmium calcium phosphate, tungsten trioxide, and zinc oxide; the first two show the greatest selectivity in respect of yield of methyl vinyl ketone. The reaction was effected at 325-400°. The yield of methyl vinyl ketone reached 87% on reacted vinylacetylene, with a 31.8% conversion. By-products obtained were methyl vinyl ketone dimer (3-4%) and a polymer of vinylacetylene (1-1.5%).

Hydration of isopropenylacetylene produces isopropenyl methyl ketone in a yield of up to 91%, [187-190] but because of the poor availability of the starting isopropenylacetylene this method has no commercial value.

The process is thus of commercial value only for the production of methyl vinyl ketone.

2. Production of α,β-Unsaturated Ketones by the Aldol Condensation of Formaldehyde with Saturated Ketones

This method is analogous to the corresponding method for the production of α,β-unsaturated aldehydes, and can similarly be carried out in vapour or liquid phase.

The vapour-phase condensation is conducted at 250–450° in the presence of catalysts: lead zeolite catalysts[191]; silica gel[149,192]; silica gel impregnated with a 1% solution of NaOH, KOH, or RbOH[149,192]; alumina containing oxides of zirconium, cerium, thorium, zinc, or magnesium[193]; industrial KDS catalyst [catalyst used in synthetic rubber production(Ed. of Translation)][194]; Cd, Ca phosphate[194]; rare-earth oxides[194]; and various natural clays[194]. The reactant ratios employed vary, according to different sources of data, from equimolar[194] to a four-fold excess of acetone[191]. This method has produced the following ketones, in the yields indicated: methyl vinyl ketone (40–99%)[191,192,194], isopropenyl methyl ketone (28–97%)[191,192], 1-isopropylvinyl methyl ketone (86.6%)[191], 1-ethylvinyl methyl ketone (22.6%)[192], and phenyl vinyl ketone (77.5%)[191] as well as others.

The main disadvantage of this method is that the resulting vinyl ketones are contaminated with formaldehyde and various by-products, such as hydrocarbons, alcohols, and resins. Moreover, the vinyl ketones obtained by the vapour-phase process give, on polymerisation, unstable and irreproducible results; often coloured gels with various inclusions are obtained, instead of colourless transparent solid polymers. This has been shown to be due to the presence of impurities which are difficult to remove[190].

The liquid-phase condensation is of much greater value, and has been used for the production of isopropenyl methyl ketone on an industrial scale[31].

The aldol condensation of formaldehyde with acetone:

$$CH_3COCH_3+CH_2O \rightarrow CH_3COCH_2CH_2OH \xrightarrow{-H_2O} CH_3COCH=CH_2.$$

takes place at pH 8.5–9.5 in an aqueous or alcoholic medium. The total yield of methyl vinyl ketone obtained in aqueous medium is 10–18%.[195-198] Higher yields (up to 50% of theory) may be obtained in an aqueous medium with a higher ratio of acetone to formaldehyde (up to 30 : 1)[199,200]. The catalyst is sodium hydroxide, in amount not exceeding 0.5–0.8 wt. % of the reaction mixture; the use of more sodium hydroxide produces a yellow viscous mass insoluble in water[32]. Recent studies of the influence of the reaction conditions on the aldol condensation of acetone with formaldehyde[201-203] indicate that the optimum yield of 1-hydroxybutan-3-one, and hence of methyl vinyl ketone (up to 65% of theory), is obtained by using a fourfold excess of acetone at 40–45° in an alcoholic medium.

The aldol condensation of formaldehyde with acetone is a very complex reaction, and the nature of the final products depends on the reactant ratio employed. By-products obtained are 4-hydroxy-4-methylpentan-2-one (4–5%), 2-hydroxybut-1-en-3-one (14–15%), 1,3-dioxan-5-yl methyl ketone (3–4%), and 1,3-dioxan-5-yl isobutenyl ketone (10–11%)[196], and also resinous high-molecular polymers of the enol form of the hydroxybutanone[131].

Because of the large amounts of by-products and the low yields of methyl vinyl ketone, this method has no commercial value.

Isopropenyl methyl ketone is obtained more smoothly:

$$CH_3COCH_2CH_3+CH_2O \xrightarrow{NaOH} CH_3COCH(CH_2OH)CH_3 \xrightarrow[-H_2O]{} CH_2=\overset{CH_3}{\underset{|}{C}}-COCH_3+H_2O.$$

This reaction was investigated by Staudinger and Ritzenhalter[204] and later by Morgan *et al.*[32]; the latter found excess of formaldehyde to be as harmful in the reaction with ethyl methyl ketone as in the reaction with acetone.

Best yields of isopropenyl methyl ketone are obtained by using the reagents in the proportions 11 moles ethyl methyl ketone, 10 moles formaldehyde, and 0.02 mole NaOH. The reaction mixture is initially heated to 50–60°, and then because of the exothermic nature of the reaction it is cooled to 20–25°. During the condensation the formaldehyde can undergo the Cannizaro reaction under the influence of the alkali, and so it is necessary to continue adding alkali to maintain the pH of the medium constant. The yield of 1-hydroxy-2 methylbutan-3-one is 82.7% and 42% on reacted ethyl methyl ketone and formaldehyde respectively.

The resulting 1-hydroxy-2-methylbutan-3-one is readily dehydrated to isopropenyl methyl ketone by distillation in the presence of oxalic acid[31,205]. Other dehydrating agents (iodine, potassium hydrogen sulphate, zinc chloride, etc.) are not recommended for extensive use, since they reduce the optical quality of the polymerisation product[31]. The yield of isopropenyl methyl ketone is ~80%, based on the hydroxybutanone; the optimum overall yield of isopropenyl methyl ketone is thus ~66% based on ethyl methyl ketone, and ~33% based on formaldehyde. The yield of isopropenyl methyl ketone based on formaldehyde has since been considerably improved (to 55%)[206]. Conditions have been found[37-39] for obtaining the hydroxybutanone in 87% yield, and according to a patent[205] this can be decomposed to give a 95% yield of isopropenyl methyl ketone.

It has recently been recommended[207,208] to carry out the condensation in the presence of triethylamine (pH of the mixture 10.8–11.0) with a ratio of ethyl methyl ketone to formaldehyde of 30 : 1; at 80° and a pressure of 3.2 at [1 at = 0.968 atm (Ed. of Translation)], reaction is complete in 16 min. The dehydration is accomplished in the presence of 5% aqueous phosphoric acid in a distillation column. The isopropenyl methyl ketone is obtained in a yield of up to 86.6% of theoretical, together with ethyl vinyl ketone (less than 8%) and traces of isopropenyl vinyl ketone.

Attempts to condense formaldehyde with aliphatic aromatic ketones in the liquid phase in the presence of alkaline or acid catalysts have been unsuccessful[175], but relatively recently it was reported[209] that phenyl 1-phenylvinyl ketone is obtained in 75% yield by the reaction of benzyl phenyl ketone with excess of paraformaldehyde in the presence of alkali.

The liquid-phase aldol condensation at present is seen to have a certain commercial value only for the production of isopropenyl methyl ketone.

3. Production of α,β-Unsaturated Ketones by the Mannich Reaction between Formaldehyde and Saturated Ketones

Even Mannich himself[210,211] indicated the possibility of obtaining α,β-unsaturated ketones by reacting formaldehyde, a secondary amine hydrochloride and saturated

ketones to produce hydrochlorides of Mannich bases followed by decomposition to the vinyl ketone and the secondary amine hydrochloride. With methyl vinyl ketone the reactions are:

$$CH_3COCH_3+CH_2O+R_2NH\cdot HCl \longrightarrow CH_3COCH_2CH_2NR_2\cdot HCl+H_2O,$$
$$CH_3COCH_2CH_2NR_2\cdot HCl \longrightarrow CH_3COCH=CH_2+R_2NH\cdot HCl.$$

There have since been several papers [158,212-221] and a patent [222] on the production of α,β-unsaturated ketones by this method. The main disadvantage of the process until now, as in the production of α,β-unsaturated aldehydes, has been the poor reproducibility of the Mannich reaction, which has prevented wide application of the method even for preparative purposes. For instance, in 1949 Hagemeyer [214] reported the production of methyl vinyl ketone and isopropenyl methyl ketone in yields of 80.5% and 81.9% respectively. Subsequently some workers [215,216] have confirmed Hagemeyer's yields, while others [223,224] have obtained low yields of the vinyl ketones. Clearly the reaction conditions suggested by Hagemeyer do not ensure a reproducible process.

This deficiency has been made good by Farberov and coworkers [171-173,225,226], who have made this process commercially feasible. Their detailed study of the Mannich reaction with a number of ketones has ensured complete reproducibility of experiments and a high rate of reaction, so that α,β-unsaturated ketones can be obtained in high yields (82-95%) and in a relatively short time. As already stated, in the synthesis of methacrolein and other α-substituted acroleins by the Mannich reaction the pH of the reaction mixture has an exceptional influence on the rate of reaction, the latter being satisfactory only at pH 6-7. The pH of the reaction mixture is of even greater importance in the production of α,β-unsaturated ketones, since it affects not only the rate of the Mannich reaction, but also the yield of the Mannich base reaction products, and consequently the yield of α,β-unsaturated ketones. The Mannich reaction with ketones proceeds at a satisfactory rate only at low pH values; at pH 6-7 (the optimum range for the production of methacrolein) a Mannich base is not formed. At 100° and pH 1 there is quantitative conversion of the starting materials in 1.5-2.0 h.

In our opinion [171,172] this dependence of the rate of aminomethylation on the pH of the medium indicates that the reaction proceeds by several different mechanisms. The Mannich reaction with aldehydes, which is accelerated by increase of pH, apparently proceeds by a nucleophilic substitution mechanism (S_N2) with intermediate formation of a carbanion by abstraction of a proton from the aldehyde. The Mannich reaction with ketones, which is accelerated by decrease of pH, proceeds by an electrophilic substitution mechanism (S_E2) with intermediate formation of a carbonium-imonium ion $[R_2N-\overset{+}{C}H_2 \leftrightarrow \leftrightarrow R_2\overset{+}{N}=CH_2]$, which is in fact the aminomethylating agent in this case.

The hydrochlorides of the Mannich bases obtained with ketones are more stable to heat than those obtained with aldehydes; the latter are decomposed to form unsaturated aldehydes on heating the aqueous solution to 90-100°, while the former require temperatures of the order of 150-200°. To decrease losses of the vinyl ketones by polymerisation the decomposition has been carried out under vacuum. Technological processes have been developed in principle for the production of methyl vinyl ketone and isopropenyl methyl ketone.

Recent work has thus shown that α,β-unsaturated ketones can be obtained by the Mannich reaction between formaldehyde and ketones in yields close to theoretical. Advantages of this process are the practically complete conversion of the starting materials per pass, the simplicity of the apparatus, the high yields of the vinyl ketones, and the absence of side reactions, which considerably simplifies the isolation of the vinyl ketones formed. Because of all this the process can be readily worked industrially.

This method has been employed for the production of methyl vinyl ketone [214,217,222], isopropenyl methyl ketone [214,215,222], 2-thienyl vinyl ketone [158], isopropenyl 2-thienyl ketone [158], phenyl vinyl ketone [158,212,217,221], isopropenyl phenyl ketone [213,218,222], 1-ethylvinyl phenyl ketone [213], isopropenyl ethyl ketone [215], 1-isopropylvinyl methyl ketone [215], *m*- and *p*-nitrophenyl vinyl ketones [219,220], and others.

In subsequent work Farberov and coworkers [172,226] have used the Mannich reaction to develop a new method for the production of divinyl ketones, which are of considerable interest as cross-linking agents for high-molecular compounds and as starting materials for other syntheses.

The Mannich reaction is applicable to the production of a large number of carbonyl monomers [168-173,224-226], and this is another advantageous feature of the process.

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CATALYTIC REDUCTION OF DINITRILES

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I. INTRODUCTION

As a result of the extensive industrial applications of the polymeric condensation of bifunctional compounds, a great deal of research has been done in recent years on methods of preparation of diamines. Of these, the catalytic reduction of dinitriles to diamines seems to hold the greatest promise.

Several papers have also been published on the partial reduction of dinitriles. The preparation of ω-amino-acid nitriles by catalytic hydrogenation of dinitriles may become important as a simple route to ω-amino-acids and lactams, particularly caprolactam.

In spite of the many patents and papers on the catalytic reduction of dinitriles, the field has not been reviewed up to the present.

II. REACTION CONDITIONS

The hydrogenation conditions of aliphatic, aromatic, and organosilicon dinitriles are summarised in Table 1. The reduction catalyst used is invariably a Group VIII metal: palladium activated by platinum oxide[1], Raney nickel and cobalt[2-33], nickel and cobalt catalysts on a carrier[34-39], and also nickel boride[40,41] and cobalt boride[41,42] catalysts, prepared by reduction to the metal of a salt in aqueous solution, using sodium tetrahydroborate[42].

In the presence of noble metals, the reaction proceeds rapidly at room temperature and under hydrogen pressures close to 1 atm.[1] Nickel and cobalt catalysts require elevated temperatures and hydrogen pressures. The dinitrile of adipic acid can be hydrogenated under milder conditions on a Raney nickel than on a Raney cobalt catalyst[7,8]. Cobalt catalysts are the more stable, and the more selective towards formation of a primary diamine. Raney nickel retained its activity for 30–35 h without regeneration[7] in the reduction of the adipodinitrile under flow conditions, whereas Raney cobalt and Co/Al_2O_3 retained it for ~ 500 h.[8,39]

Raney nickel–copper catalysts were found to be appreciably less active towards hydrogenation of the adipodinitrile[46]. Raney iron also has a low catalytic activity: the dinitrile of terephthalic acid is reduced to a negligible extent in the presence of this catalyst[13]. Thus the activity of metallic catalysts towards the reduction of dinitriles decreases in the sequence: Pt, Pd > Ni > Co > Fe, Cu. The reaction is usually carried out in the liquid phase, in a medium of ammonia[2-8,18-43] or of an inert solvent (alcohol, dioxan) saturated with ammonia[9-17].

By studying the catalytic reduction of the dinitriles of adipic, sebacic, terephthalic, isophthalic, and *p*- and *m*-phenylenediacetic acids it has been shown that an ammoniacal medium favours the formation of primary amines and lowers the yield of secondary and tertiary amines[10-12,17].

However, the reduction of the second nitrile group of adipodinitrile is hindered[3] at very high concentrations of ammonia, and a significant amount of the partial hydrogenation product (6-aminocapronitrile) is formed in addition to hexamethylenediamine.

In a solution of sodium acetate in acetic anhydride at 50° and under a hydrogen pressure of 3.5 atm, hexamethylenediamine was formed on Raney nickel in almost quantitative yield, but the catalyst rapidly lost its activity and disintegrated. Under the same conditions, the yield of

hexamethylenediamine was 77% and 25% on Raney Ni–Cr and Co catalysts respectively[5]. The low yield of diamine on the cobalt catalyst suggests that the reaction conditions (temperature and hydrogen pressure) were not the most favourable.

A primary diamine is either not formed at all[43], or is obtained in negligible yield[21,41,43], in the hydrogenation of dinitriles containing 2–3 carbon atoms between the nitrile groups.

There have been isolated studies of the catalytic reduction of dinitriles in the vapour phase. Under these conditions the reaction attacks the nitrile group with formation of a hydrocarbon and ammonia. Thus, 46% of *p*-xylene and 11% of *p*-tolunitrile were obtained[44] in the vapour-phase hydrogenation of the dinitrile of terephthalic acid on kieselguhr-supported Ni–Cu catalysts.

The formation of aminonitriles from dinitriles is observed when the hydrogenation is conducted under conditions milder than required to give the diamines. Therefore, the nitrile groups are reduced successively.

The conditions leading to partial reduction of diamines are set out in Table 2. It can be seen that aminonitrile formation is favoured by moderate hydrogen pressure[2] and temperature[45], high dilution with solvent[2,3], the use of low-activity Raney nickel (partly deactivated by treatment with water vapour under pressure[46] or with addition of copper or

TABLE 1.

Dinitrile	Catalyst	Medium*	Temperature, °C	Hydrogen pressure, atm	Yield of diamine, %	Reference
1	2	3	4	5	6	7
NC—$(CH_2)_3$—CN	Ni, Raney	ammonia, 7	140	120	20	21
NC—$(CH_2)_2$—CN	Ni, Raney	ammonia, 5	70	125	5	40
NC—$(CH_2)_3$—CN	Co, Raney	alcohol, 1, and ammonia, 5	100	120	55	41
NC—$(CH_2)_3$—CN	Co, Al_2O_3	ammonia, 18	125	240	42	22
NC—$(CH_2)_3$—CN	Co–kieselguhr	methanol, 0.2, and ammonia, 23	125	210	41	22
NC—$(CH_2)_4$—CN	Pd–PtO	abs. alcohol or dioxan + + H_2SO_4	room	1.6	70—80	1
NC—$(CH_2)_4$—CN	Pd–PtO	abs. alcohol or dioxan + + HCl	room	1.6	98	1
NC—$(CH_2)_4$—CN	Ni, Raney	butanol, 15	100—110	80—100	83—85	2
NC—$(CH_2)_4$—CN	Ni–Co, Raney	ammonia, 2–4	170—190	100	70	3
NC—$(CH_2)_4$—CN	Ni–Fe–Mo, Raney	ammonia, 2–4	170—190	100	70	3
NC—$(CH_2)_4$—CN	Ni, Raney	ammonia, 5–6	90—140	70	82	4
NC—$(CH_2)_4$—CN	Ni, Raney	ammonia, 3	80	100	78	41, 56
NC—$(CH_2)_4$—CN	Ni, Raney	no ammonia	80	100	52	56
NC—$(CH_2)_4$—CN	Ni, Raney	$(CH_3CO)_2O$ + NaOH	50	3.5	100	5
NC—$(CH_2)_4$—CN	Ni–Cr, Raney	$(CH_3CO)_2O$ + NaOH	50	3.5	77	5
NC—$(CH_2)_4$—CN	Co, Raney	$(CH_3CO)_2O$ + NaOH	50	3.5	25	5
NC—$(CH_2)_4$—CN	Co, Raney	methanol, 3, and ammonia, 2	85—90	100	80—85	8
NC—$(CH_2)_4$—CN	Co, Raney	ammonia, 2	110	110	94	41, 56
NC—$(CH_2)_4$—CN	Co, Raney	no ammonia	120	110	74	56
NC—$(CH_2)_4$—CN	Ni–MgO	ammonia, 3	80	120	78	56
NC—$(CH_2)_4$—CN	Ni–MgO	no ammonia	90	115	40	56
NC—$(CH_2)_4$—CN	Co–MgO	no ammonia	120	120	60	56
NC—$(CH_2)_4$—CN	Ni, alumina–silica	ammonia, 3	110	120	40	56
NC—$(CH_2)_4$—CN	Ni, alumina–silica	no ammonia	80	120	25	56
NC—$(CH_2)_4$—CN	Ni–SiO_2	ditto	100	100	17	75
NC—$(CH_2)_4$—CN	Ni–WO_2	»	95	100	24	75
NC—$(CH_2)_4$—CN	Ni–ZrO_2	»	95	100	8	75
NC—$(CH_2)_4$—CN	Ni–TiO_2	»	95	100	7	75
NC—$(CH_2)_4$—CN	Ni–Al_2O_3	»	95	100	6	75
NC—$(CH_2)_4$—CN	Ni boride	ammonia, 3	120	120	75	41
NC—$(CH_2)_4$—CN	Co boride	ammonia, 2	100	110	90—94	42, 41
NC—$(CH_2)_4$—CN	Co boride	no ammonia	100	110	71	42
NC—$(CH_2)_4$—CN	Ni boride–MgO	ditto	80	100	61	75
NC—$(CH_2)_4$—CN	Ni boride–WO_3	»	85	100	54	75
NC—$(CH_2)_4$—CN	Ni boride–MoO_3	»	85	100	28	75
NC—$(CH_2)_4$—CN	Ni boride–MoO_3–Al_2O_3	»	80	100	35	75
NC—$(CH_2)_4$—CN	Ni, Raney	ammonia, 2	50	80**	75	7
NC—$(CH_2)_4$—CN	Co, Raney	ammonia	80—85	200**	90—95	8
NC—$(CH_2)_4$—CN	Co–Al_2O_3	ammonia, 27	100	200**	95	39
NC—$(CH_2)_3$—CH (OCH_3)—CH_2—CN	Co, Raney	ammonia	not stated		90	6
NC—$(CH_2)_3$—CH (OC_4H_9)—CH_2—CN	Co, Raney	ammonia	not stated		94	6
NC—$(CH_2)_6$—CN	Co, Raney	ammonia, 3–5	100	100	94	41
NC—$(CH_2)_7$—CN	Ni, Raney	ammonia, 3	100	110	91	41
NC—$(CH_2)_7$—CN	Co, Raney, or Co boride	ammonia, 3–5	100—110	100—120	95—96	41
NC—$(CH_2)_8$—CN	Ni, Raney	ammonia, 3–5	100	120	89	9, 41
NC—$(CH_2)_8$—CN	Co, Raney	ammonia, 3–5	110	120	97	41
NC—$(CH_2)_8$—CN	Ni boride	ammonia, 3–5	105	100	88	41
NC—$(CH_2)_8$—CN	Co boride	ammonia, 3–5	105	120	91	41
NC—$(CH_2)_8$—CN	Ni boride	no ammonia	105	110	65	41
NC—$(CH_2)_{10}$—CN	Ni, Raney	ammonia, 3–5	120	115	87	41
NC—$(CH_2)_{10}$—CN	Co, Raney	ammonia, 3–5	120	120	98	41
p-NC—C_6H_4—CN	Ni, Raney	dioxan, ammonia, 1	100	80	67	13
p-NC—C_6H_4—CN	Ni–Ti, Raney (24 : 1 by wt.)	n-butanol and ammonia	140—180	140	60	15
p-NC—C_6H_4—CN	Co, Raney	methanol and ammonia, 10	105	110	89	17
p-NC—C_6H_4—CN	Co, Raney	dioxan and ammonia	100—105	90	55—60	14
p-NC—C_6H_4—CN	Co, Raney	methanol and ammonia	100—105	90	75—77	14
p-NC—C_6H_4—CN	Co, Raney	aqueous NH_3 solution	60—140	105—200	80	96
p-NC—C_6H_4—CN	Ni–Cu–kieselguhr	***	304	atmospheric	0	44
m-NC—C_6H_4—CN	Ni, Raney	dioxan and ammonia, 3	100	100	79	43
m-NC—C_6H_4—CN	Co, Raney	methanol and ammonia	100	100	61—75	18
m-NC—C_6H_4—CN	Co, Raney	methanol and ammonia	100	140	84	18
m-NC—C_6H_4—CN	Co, Raney	no ammonia	100	100	30	18
m-NC—C_6H_4—CN	Co, Raney	aqueous NH_3 solution	60—140	105—200	80	96
o-NC—C_6H_4—CN	Ni, Raney	dioxan, ammonia, 3	100	100	0	43
o-NC—C_6H_4—CN	Co, Raney	dioxan, ammonia, 4	100	120	0	43
o-NC—C_6H_4—CN	Ni–Cu–kieselguhr	***	304	atmospheric	0	44

TABLE 1. (cont'd)

1	2	3	4	5	6	7
p-NC—CH_2—C_6H_4—CH_2—CN	Ni, Raney	ethanol, satd. with NH_3 at 20°	90—100	70—75	57	10
p-NC—CH_2—C_6H_4—CH_2—CN	Ni, Raney	ethanol, satd. with NH_3 at −7°	90—100	70—75	75	12
p-NC—CH_2—C_6H_4—CH_2—CN	Ni, Raney	methanol or ethanol (3 : 2)+ammonia (10 : 1)	100—105	100	64—65	17
p-NC—CH_2—C_6H_4—CH_2—CN	Co, Raney	dioxan (3 : 1)+NH_3 (10 : 1)	100—105	100	74	17
p-NC—CH_2—C_6H_4—CH_2—CN	Co, Raney****	dioxan or methanol, ammonia (10 : 1)	100—105	100	92—94	17
m-NC—CH_2—C_6H_4—CH_2—CN	Ni, Raney	ethanol, satd. with NH_3 at 20°	90—100	70—75	57	10
m-NC—CH_2—C_6H_4—CH_2—CN	Ni, Raney	ethanol, satd. with NH_3 at −7°	90—100	70—75	78.5	12
o-NC—CH_2—C_6H_4—CH_2—CN	Ni, Raney	ethanol, satd. with NH_3 at 20°	90—100	70—75	0	10
o-NC—CH_2—C_6H_4—CH_2—CN	Ni, Raney	ethanol, satd. with NH_3 at −7°	90—100	70—75	20	11
$(CH_3)_2Si(C_6H_4CN)_2$	Ni, Raney	ammonia	125—130	350	26	19
[NC—CH_2—CH_2—Si $(CH_3)_2$]$_2$O	Ni, Raney	alcohol, 1, and ammonia, 5	80	110	89	92
[NC—CH_2—CH_2—Si $(CH_3)_2$]$_2$O	Co, Raney	alcohol, 1, and ammonia, 5	80	120	92	92
[NC—CH_2—CH_2—Si $(C_2H_5)_2$]$_2$O	Co, Raney	ammonia, 12	80	110	63	92
[NC—CH_2—CH_2—Si $(OC_2H_5)_2$]$_2$O	Co, Raney	absolute alcohol, 1	80	100	61	92
[NC—CH_2—CH_2—CH_2—Si $(CH_3)_2$]$_2$O	Ni, Raney	alcohol, 1, and ammonia, 2	75	100	92	20
[NC—CH_2—CH_2—CH_2—Si $(CH_3)_2$]$_2$O	Co, Raney	alcohol, 1, and ammonia, 15	100	120	95	92
[NC—CH_2—CH_2—CH_2—Si $(CH_3)(C_2H_5)$]$_2$O	Ni, Raney	alcohol, 1, and ammonia, 2.5	75	90	87	20
[NC—CH_2—CH_2—CH_2—Si $(C_2H_5)_2$]$_2$O	Ni, Raney	alcohol, 1, and ammonia, 4	70	95	70	20
[NC—CH_2—CH_2—O—CH_2—CH_2—CH_2—Si $(CH_3)_2$]$_2$O	Co, Raney	dioxan, 1, and ammonia, 3	80	115	97	92

* The amount of solvent is shown in volumes per volume of dinitrile; the amount of NH_3 in moles per mole of dinitrile.

** Reaction carried out in a flow system.

*** Reaction carried out in the vapour phase.

**** The "cold leaching out" method was used[98].

TABLE 2.

Dinitrile	Catalyst	Medium*	Temperature, °C	Initial hydrogen pressure, atm	Yield, wt. % aminonitrile	Yield, wt. % diamine	Reference
Adipic NC—$(CH_2)_4$—CN	Ni, Raney	butanol, 15	75—80	1.5—1.7	90	**	2
NC—$(CH_2)_4$—CN	Ni, Raney	butanol, 15	75—80	1.5—1.7	50	25	48
NC—$(CH_2)_4$—CN	Ni, Raney	methanol, dioxan, or without solvent	room	5	38—51	20	45
NC—$(CH_2)_4$—CN	Ni, Raney	methylal, methanol, or dioxan, 6, ammonia, 1.9	100	70	48	5	97
NC—$(CH_2)_4$—CN	Ni, Raney treated with water vapour at 350°	ammonia, 2.5	80	100	58	14	46
NC—$(CH_2)_4$—CN	Ni–Ti, Raney, 43 : 7 by wt.	ammonia, 2	80	100	57	17	40
NC—$(CH_2)_4$—CN	Ni–Ti, Raney, 3 : 2 by wt.	ammonia, 2	60—80	100	51	13—14	40
NC—$(CH_2)_4$—CN	Ni–Ti, Raney, 12 : 1 by wt.	ammonia, 2	60	20	60	3	40
NC—$(CH_2)_4$—CN	Ni–Cu, Raney, 1 : 4 by wt.	ammonia, 5	80	100	56	16	46
NC—$(CH_2)_4$—NC	Fe–Cu, Raney, 1 : 1 by wt.	ammonia, 4.5	80	100	53	12	46
NC—$(CH_2)_4$—CN	Fe–Co, Raney, 19 : 1 by wt.	ammonia, 4	120	140—210	68	6	99
NC—$(CH_2)_4$—CN	Ni–Al_2O_3	ammonia, 4	120	140	52	22	23
NC—$(CH_2)_4$—CN	Ni–kieselguhr	ammonia, 4	120	140—210	51	17	47
NC—$(CH_2)_4$—CN	Ni-boride	ammonia, 2	80	100	61	3	40
NC—$(CH_2)_4$—CN	Co boride	ammonia, 3	80	100	41	17	40

TABLE 2. (contd)

Dinitrile	Catalyst	Medium*	Temperature, °C	Initial hydrogen pressure, atm	Yield, wt. % aminonitrile	Yield, wt. % diamine	Reference
NC—$(CH_2)_4$—CN	Co–kieselguhr	ammonia, 4	120	140—210	52	42	99
Pimelic NC—$(CH_2)_5$—CN	Ni, Raney Co–kieselguhr	methanol or dioxan,	room	5	40	30	45
NC—$(CH_2)_5$—CN		ammonia, 4	120	175	25	**	47
Azelaic NC—$(CH_2)_7$—CN	Ni, Raney	methanol, dioxan, or without solvent	room	5	21—25	20—30	45
Sebacic NC—$(CH_2)_8$—CN	Fe–Co, Raney, 12 : 2 by wt.	ammonia, 4	120	105—175	24	37	99
NC—$(CH_2)_8$—CN	Ni–Al_2O_3	ammonia, 4	120	140	20	**	23

* The amount of NH_3 is given in moles per mole of dinitrile; the amount of solvent in volumes per volume of dinitrile.

** Yield not stated.

titanium[40,46]), the use of a nickel catalyst on a carrier[23,47], and lastly the use of nickel boride or cobalt boride catalysts[40]. Aminocapronitrile was obtained also when the reaction was carried out in the presence of insufficient catalyst[4].

Reductions on nickel and cobalt catalysts under static conditions usually give significant amounts of diamine (up to 40%) in addition to aminonitrile (25–60%) even before the absorption of sufficient hydrogen to reduce one nitrile group[45-47]. Reduction on a chromium-modified nickel boride catalyst is more selective: the yields are 61% of 6-aminocapronitrile and 3% of diamine. However, hydrogen absorption on this catalyst ceased before the whole of the dinitrile had reacted.

It has been suggested that further hydrogenation is greatly retarded by dilution of the dinitrile because of desorption

from the catalyst surface by the resulting aminonitrile. In the presence of hexamethylenediamine the extent of conversion of the dinitrile is also decreased. Reduction of the second nitrile group begins at higher temperatures [40].

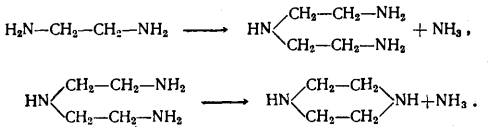
Stepwise hydrogenation of the dinitrile of adipic acid has been carried out also under flow conditions, using a nickel–titanium–alumina catalyst. The relative amounts of aminonitrile and diamine in the product were found to depend strongly on the flow rate of the dinitrile [46]. Under optimum conditions (temperature 60°, hydrogen pressure 20 atm, flow rate of dinitrile 45 ml h^{-1}) the yield of 6-aminocapronitrile was ~ 60%, and that of hexamethylenediamine only 9%.

III. DEAMINATION OF PRIMARY AMINES

It has been stated that secondary amines are formed during catalytic reduction of dinitriles by the deamination of primary amines [3,4]. Thus, secondary amines were obtained [49,50] by refluxing solutions of benzylamine or 2-phenylethylamine in the presence of palladium black, whereas reduction of benzonitrile and phenylacetonitrile on the same catalyst but under milder conditions (at 35°) gave primary amines [50].

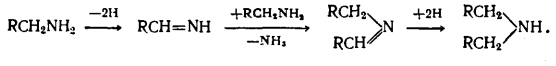
Martin and Martell [51] prepared piperazine by heating ethylenediamine and diethylenetriamine to 150–160° in the presence of Raney nickel. The deamination of diethylenetriamine in xylene, tetralin, dipentene, and without a solvent gave piperazine in yields of 17, 62, 73, and 53% respectively.

From ethylenediamine in a tetralin medium, piperazine was obtained in 39% yield. The authors suggest that diethylenetriamine is formed first, and converted into piperazine:



Heating tetramethylenediamine to 160° in the presence of nickel on kieselguhr gave pyrrolidine in 87% yield [52]. Piperidine was obtained in 62% yield [53] by the same method from pentamethylenediamine heated to 400° in the presence of acidic catalysts (SiO_2, Al_2O_3–SiO_2, BPO_4). A method has also been proposed [54] for the catalytic production of hexamethyleneimine [perhydroazepine (Ed. of Translation)] from hexamethylenediamine at temperatures above 200°.

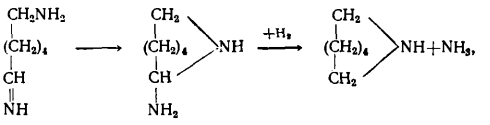
Kindler [55] suggested that aminoaldimines are involved as intermediates in the phytosynthesis of pyrrolidines and piperidines from diamines, and proposed a general scheme for the formation of secondary from primary amines:



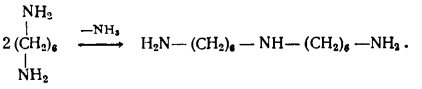
The H_2N-CH_2 group is dehydrogenated, then a Schiff's base is produced from the resulting aldimine, and the amine, and lastly the Schiff's base is hydrogenated.

Zil'berman and Skorikova [4] prepared a mixture containing 20% hexamethyleneimine, 63% hexamethylenediamine, and 17% of a high-boiling residue, by refluxing hexamethylenediamine for 12 h in the presence of a Raney nickel catalyst. On raising the reduction temperature of the adipodinitrile and extending the reaction time, the yield of hexamethylenediamine fell and that of the high-boiling residue (mainly bishexamethylenetriamine) increased. However, the yield of hexamethyleneimine remained almost constant.

The authors conclude that the cyclic secondary amine, hexamethyleneimine, is formed through an aldimine:



and that the secondary straight-chain amine, bishexamethylenetetramine, is formed by deamination of the diamine:



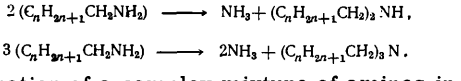
Freidlin and Sladkova [56] showed that on Raney nickel under the optimal conditions for the reduction of adipodinitrile to hexamethylenediamine (temperature 80–100°, hydrogen pressure 100 atm), hexamethylenediamine does not undergo deamination, and that under these conditions bishexamethylenetriamine and hexamethyleneimine are unchanged and do not interact. Deamination of hexamethylenediamine was observed at 140° on Raney nickel, at 160° on Raney cobalt, and at 200° on Ni/MgO. On Raney nickel the yield of hexamethyleneimine reached 32%, that of *N*-(6-aminohexyl)hexamethyleneimine reached 29%. The authors conclude from their results that the formation of secondary and tertiary amines during catalytic reduction of the dinitrile of adipic acid to hexamethylenediamine, under optimal conditions, occurs by the aldimine mechanism, and not by deamination of the primary diamine.

Thus, the optimal deamination temperature for primary amines is higher than the reduction temperature of nitriles to primary amines.

IV. MECHANISM OF THE CATALYTIC REDUCTION OF NITRILES

1. Mechanism of Reduction of Mononitriles

Sabatier and Senderens [57] obtained a mixture of primary, secondary, and tertiary amines by catalytic reduction of nitriles on a nickel catalyst at 180–350°. At the higher temperatures the yield of secondary and tertiary amines increased, and appreciable formation of hydrocarbons and evolution of ammonia was observed. The authors consider that the secondary and tertiary amines are formed by deamination:



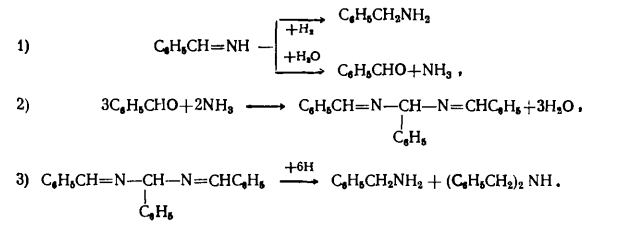
The formation of a complex mixture of amines in the catalytic hydrogenation of nitriles has been repeatedly observed [58,59].

Rosenmund and Pfankuch [60] were the first to carry out the process in an acid medium in order to discourage the formation of secondary amines: they obtained primary amines in 80% and 73% yield from benzonitrile and phenylacetonitrile respectively, using a $Pd/BaSO_4$ catalyst and

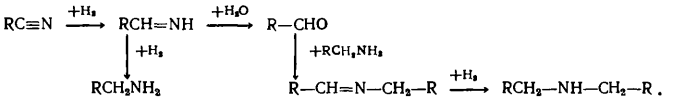
a glacial acetic acid medium. According to the authors[60], the acid reacts with the primary amine as it forms, and protects it from deamination to secondary and tertiary amines. Carothers and Jones[61] also obtained exclusively primary amines (as their acetyl derivatives) by the reduction of aromatic nitriles on Adams platinum in an acetic anhydride medium.

The use of strong acid media, though successful with platinum and palladium catalysts, is not permissible with nickel and cobalt catalysts, because these are severely attacked and lose their activity under these conditions[5,62].

Paal and Gerum[58] put forward the suggestion that the catalytic reduction of nitriles proceeds through the stage of aldimine formation, and that the formation of a secondary amine does not occur by deamination of a primary amine. The aldimine is partially hydrolysed to an aldehyde, which then reacts with ammonia to give a bis-Schiff's base. Hydrogenation of the latter produces a primary and a secondary amine:



A comparison of the composition of the hydrogenation products of benzonitrile and phenylacetonitrile on a nickel catalyst, with and without added phenylhydrazine, led Rupe and Hodel[63] to the conclusion that only step (1) can be correct in the above scheme. Formation of a bis-Schiff's base was not observed. It was also shown that the Schiff's base (benzylideneaniline) is reduced easily and almost quantitatively, under similar conditions, to a secondary amine. Hence, the authors consider that the primary amine is obtained exclusively through an aldimine, whilst the secondary amine is obtained through a Schiff's base, whose formation requires the conversion of the aldimine into an aldehyde:

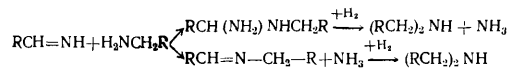


The conversion of the intermediate aldimine into an aldehyde was observed by Pietra and Trinchera[64] in the course of the reduction of aromatic nitriles on Raney nickel in aqueous-alcoholic media containing hydrazine (to precipitate the aldehydes as their hydrazones). The yield of aldehydes from benzonitrile, *o*-, *m*-, and *p*-tolunitriles, 1- and 2-naphthonitriles, was 81, 78, 82, 82, 69, and 59% respectively.

Plieninger and Werst[65] obtained aldehyde semicarbazones during hydrogenation of aliphatic and aromatic nitriles on Raney nickel and cobalt catalysts in water or aqueous alcoholic media.

Rupe and Becherer[66] obtained a Schiff's base in 70% yield during reduction of 2-naphthonitrile on a nickel catalyst in aqueous alcohol. The base was not hydrogenated to a secondary amine because it was sparingly soluble under the reaction conditions. The hydrogenation of 1-naphthonitrile under similar conditions did not produce the corresponding Schiff's base because the latter, being readily soluble, was reduced to a secondary amine. The authors' explanation for the absence of Schiff's bases among the reduction products of other nitriles is that they are usually very soluble and are therefore hydrogenated to secondary amines.

The scheme of formation of secondary amines involving reaction between an aldimine and an aldehyde was not applicable to the reduction of nitriles in anhydrous media. Yet, Braun *et al.*[67] obtained a mixture of primary and secondary amines even from the hydrogenation of nitriles in non-aqueous media. The relative yields depended on the nature and the concentration of the solvent. Hence the authors suggest that the primary amine is formed from an aldimine, whilst the secondary amine is formed by the condensation of the aldimine with the primary amine:

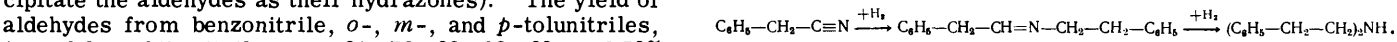


In the presence of a solvent, the formation of a secondary amine could be expected to decrease, owing to the lower probability of interaction between the aldimine and the primary amine. The experimental results were in keeping with this proposition. When the concentration of benzonitrile in decalin (or tetralin) was increased from 34% to 91% the yield of benzylamine rose from 44% to 72% and the yield of *N*-phenylbenzylamine fell from 40% to 5%. In n-pentanol, the same concentrations of nitrile produced 59% and 14% of the primary amine and 71% and 8% of the secondary amine respectively. A similar variation of the yield of primary amine with nitrile concentration was observed also in the reduction of phenylacetonitrile, 1- and 2-naphthonitriles, and *o*-, *m*-, and *p*-tolunitriles. However, the formation of a condensation product between an aldimine and a primary amine, or of a Schiff's base, was not demonstrated experimentally in this work.

Carothers and Jones[61], whilst carrying out the reduction of benzonitrile and *p*-tolunitrile over Adams catalyst in absolute alcohol, also obtained mixtures of primary and secondary amines.

Thus, the experimental results of work on the catalytic reduction of nitriles in non-aqueous media are in agreement with the mechanism for the formation of secondary amines put forward by Braun and coworkers[67].

Kindler and Peschke[68] were the first to isolate, from the hydrogenation products of phenylacetonitrile on palladium black in an anhydrous medium, the Schiff's base *N*-(β-phenylethylidene)-2-phenylethylamine. Reduction of this compound gave di-(2-phenylethylamine):

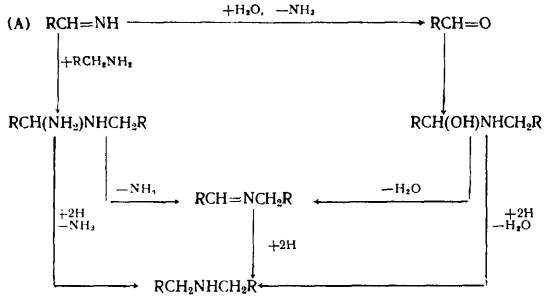


The formation of Schiff's bases in addition to primary and secondary amines during reduction of nitriles on Raney catalysts has been reported also in more recent papers.

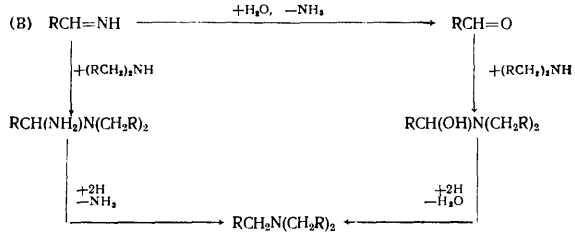
Chiavarelli and Marini-Bettolo[69] obtained 10% of a Schiff's base, besides primary (85%) and secondary amines, from the hydrogenation of 4-cyano-*N*-methyl-4-phenyl piperidine on Raney nickel.

Kindler and Hess[70] suggested possible reaction paths for the formation of secondary amines (scheme A) and tertiary amines (scheme B) during reduction of nitriles in aqueous and in anhydrous media. The secondary amine is formed by condensation of an aldimine (in anhydrous media) or an

aldehyde (in aqueous media) with the primary amine, followed by hydrogenolysis of the resulting adduct, or by conversion of the condensation product into a Schiff's base which is then hydrogenated:



Formation of the tertiary amine occurs by hydrogenolysis of the product of the condensation of an aldimine or aldehyde with the secondary amine:



Juday and Adkins[71] reduced benzonitrile on Raney nickel in the presence of aromatic amines, and obtained, among other products, a small amount of Schiff's bases mostly containing the same aromatic radical. On the other hand, the Schiff's base (and the secondary amine) obtained by hydrogenation of benzonitrile mixed with *p*-methoxybenzonitrile contained different aromatic radicals. From this the authors conclude that the formation of secondary amines during reduction of nitriles can occur, in addition to Braun's mechanism[67], by the condensation of two molecules of aldimine:

$$Ar{-}CH{=}NH + HN{=}CH{-}Ar' \rightarrow Ar{-}\underset{\displaystyle NH_2}{\underset{|}{CH}}{-}N{=}CHAr' \rightarrow$$

$$\xrightarrow[(-NH_3)]{+H_2} Ar{-}CH_2{-}N{=}CH{-}Ar' \xrightarrow{+H_2} Ar{-}CH_2{-}NH{-}CH_2{-}Ar'.$$

Many workers have examined the influence of the structure of the nitrile and of the preparative conditions on the yield of primary and secondary amines. Kindler *et al.*[72] showed that phenylacetonitrile is reduced much more slowly than benzonitrile on palladium black in glacial acetic acid or 96% ethanol. Secondary amines were obtained in high yield (40–68%) from phenylacetonitrile, whereas benzonitrile gave mainly the primary amine (96–99%). The authors concluded that under conditions of slow reduction of the nitrile most of the aldimine formed as an intermediate can react with the primary amine before being reduced by the hydrogen, thus giving a higher yield of secondary amine.

Winans and Adkins[73] also came to the conclusion that secondary amines can be formed by two different paths during the catalytic reduction of nitriles: deamination of two molecules of the primary amine, and reaction between an aldimine and the primary amine by Braun's mechanism[67]. Deamination of primary amines (n-pentylamine, cyclohexylamine, 2-phenylethylamine) in the presence of a nickel catalyst was carried out[73] above 160–170°. The authors point out that a catalyst is unnecessary for the formation of a Schiff's base from an aldimine and an amine, and that this reaction occurs even at room temperature, so that, in order to obtain a high yield of primary amine, nitriles should be reduced under conditions which favour hydrogenation, namely, in the presence of sufficient catalyst and under high hydrogen pressures and temperatures.

More recently, Schwoegler and Adkins[74] have suggested a more effective method of raising the yield of primary amines. On the basis of Braun's scheme for the formation of secondary amines, they point out that the yield of secondary amines should decrease in the presence of ammonia, which can react with the aldimine:

$$RCH{=}NH + NH_3 \longrightarrow \underset{\displaystyle NH_2}{\overset{\displaystyle NH_2}{\underset{|}{\overset{|}{RCH}}}} \xrightarrow{+H_2} RCH_2NH_2 + NH_3.$$

The authors confirmed this suggestion experimentally. The formation of secondary amines was almost completely suppressed when they reduced the nitriles of n-butyric acid and n-heptanoic acid in the presence of ammonia. The method has, since then, become extensively used.

Thus, a great deal of experimental work supports the conclusion that the catalytic reduction of aliphatic and aromatic mononitriles to primary and secondary amines occurs by an aldimine mechanism. At high temperatures, secondary amines can be formed also by deamination of primary amines.

2. Mechanism of Reduction of Dinitriles

The formation of aminonitriles during the catalytic hydrogenation of dinitriles convincingly proves that the two nitrile groups are not reduced at the same time:

$$NC{-}(CH_2)_n{-}CN \xrightarrow{+H_2} H_2N{-}(CH_2)_{n+1}{-}CN \xrightarrow{+H_2} H_2N{-}(CH_2)_{n+2}{-}NH_2.$$

The results of many investigations point to the aldimine mechanism of reduction for both nitrile groups. Plieninger and Werst[65] hydrogenated dinitriles on Raney nickel and cobalt in aqueous or aqueous-alcoholic media in the presence of semicarbazide, and obtained the semicarbazones of the following cyanoaldehydes and dialdehydes: from the succinodinitrile, the semicarbazone of 2-cyanopropionaldehyde (yield 60%) and that of the succinodialdehyde (yield 20%); from the adipodinitrile, the semicarbazone of adipodialdehyde (yield 40%); from *o*-biscyanomethylbenzene, the semicarbazones of *o*-(cyanomethyl)phenylacetaldehyde, (yield 40%) and of *o*-phenylenediacetaldehyde (yield 20%). The formation of a cyanoaldehyde as well as a dialdehyde is additional evidence for the stepwise nature of the catalytic reduction of a dinitrile.

Thus, a primary diamine is formed by the catalytic reduction of a dinitrile through the intermediate stages of aldimine formation:

$$NC{-}(CH_2)_n{-}CN \xrightarrow{+H_2} HN{=}CH{-}(CH_2)_n{-}CN \xrightarrow{+H_2}$$

$$\longrightarrow H_2N{-}(CH_2)_{n+1}{-}CN \xrightarrow{+H_2} H_2N{-}(CH_2)_{n+1}{-}CH{=}NH \xrightarrow{+H_2} H_2N{-}(CH_2)_{n+2}{-}NH_2.$$

Published data on the effect of ammonia on the composition of the hydrogenation products of dinitriles are in agreement

with the scheme put forward by Schwoegler and Adkins[74], according to which the aldimine formed as an intermediate reacts with ammonia to give a higher yield of primary amines in the final product.

Studies of the reduction of adipodinitrile under static conditions and in the presence of different catalysts have shown that the presence of ammonia in the reaction medium favours the formation of the primary diamine.

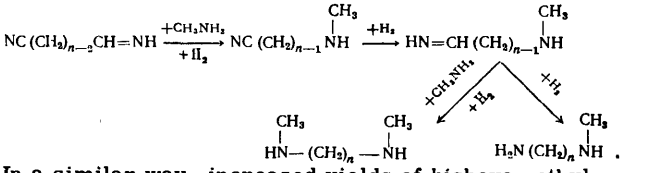
Zil'berman and Skorikova[4] established that the yield of diamine in the presence of Raney nickel is reduced from 82% to 72% by decreasing the amount of NH_3 from 9 to 3 moles per mole of dinitrile. Polkovnikov *et al.*[42] obtained hexamethylenediamine in 94% yield by the hydrogenation of adipodinitrile on a cobalt boride catalyst in the presence of ammonia: the yield fell to 71% in the absence of ammonia.

Freidlin *et al.*[75] observed a sharp increase in the yield of secondary amines, and a lower yield of hexamethylenediamine, when they carried out the reaction without ammonia on the following catalysts: Raney nickel and cobalt, nickel on magnesium oxide, and nickel on alumina–silica.

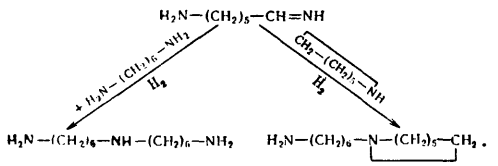
When the concentration of ammonia was increased from 10% to 20–30%, using a Raney nickel catalyst under flow conditions, the yield of hexamethylenediamine rose[7] from 40% to 65%.

The presence of ammonia in the reaction zone was found to affect the yields of primary and secondary amines in exactly the same way in the hydrogenation of adipodinitrile under flow conditions on Raney cobalt[8] and alumina-supported cobalt[39]. The yield of primary diamine has also been found to depend on the amount of ammonia present in the reaction zone in a number of investigations of the catalytic reduction of the dinitriles of terephthalic and isophthalic acids[13–16], and of the dinitriles of *p*-, *m*-, and *o*-phenylenediacetic acids[10–12] (see Table 1).

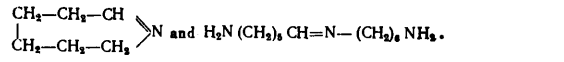
Biggs and Bishop[76], in their study of the reduction of the dinitriles of adipic and sebacic acids on Raney nickel in a medium of liquid methylamine, obtained mixed primary–secondary amines in a yield which increased with the methylamine : dinitrile molar ratio. In addition to *N*-methylhexamethylenediamine and *N*-methyldecamethylenediamine, they observed the formation of *NN'*-dimethylhexamethylenediamine and *NN'*-dimethyldecamethylenediamine. The production of mixed primary–secondary and of disecondary amines is easily explained by postulating a reaction between an aldimine and methylamine:



In a similar way, increased yields of bishexamethylenetriamine[40] and of 1,6′-aminohexylperhydroazepine[56] in the presence of added perhydroazepine have been reported for the reduction of the adipodinitrile in a medium of hexamethylenediamine:

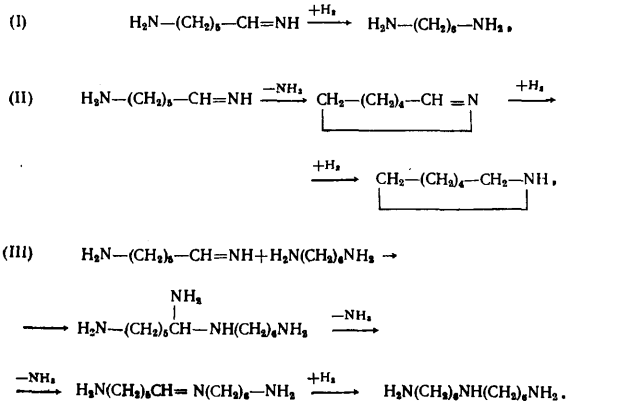


Zil'berman *et al.*[77] reported that commercial hexamethylenediamine contains small quantities of the *N*-alkylaldimines [*N*-alkylalkylideneimines (Ed. of Translation)]:

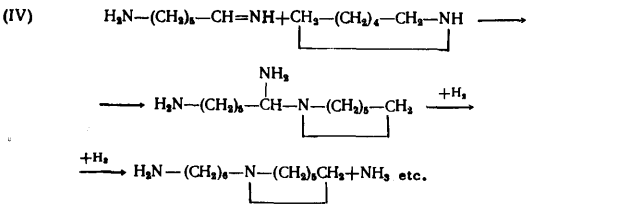


All these results indicate that secondary amines are probably formed, during catalytic reduction of dinitriles, through the stages of formation of a Schiff's base (from an aldimine and an amine) which is subsequently hydrogenated.

Secondary amine formation during reduction of dinitriles may occur either by intermolecular or by intramolecular interaction between an iminomethyl and an amino-group. Hence, cyclic as well as acyclic secondary amines can be obtained. For example, the hydrogenation of the adipodinitrile gives rise to the following amines:



A tertiary amine is formed by the reaction of an aldimine with a secondary amine:

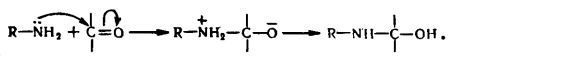


It can be seen from Eqns. (I)–(IV) that the aminoaldimine is a common intermediate product in the formation of primary, secondary, and also tertiary amines. Hence, the formation of the primary diamine and the formation of secondary and tertiary amines are competing reaction paths in the reduction of a dinitrile, and the ratio

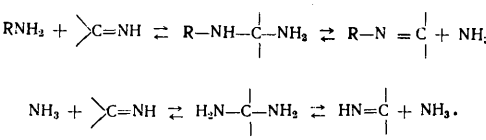
$$\frac{\text{primary amine}}{\text{sum of secondary and tertiary amines}}$$

should depend on the relative rates of the competing reactions: hydrogenation of the aldimine and addition of the aldimine to the amine (followed by hydrogenation of the resulting Schiff's base).

The formation of a Schiff's base from an aldehyde and a primary amine is known to proceed readily even at room temperature and in the absence of a catalyst[78]. The mechanism of this reaction involves attack by the base on the electrophilic carbon atom of the carbonyl group, which shifts its π electrons towards the oxygen:



In our case, there are two bases in the solution: a stronger one (the amine) and a weaker one (the ketone). The reaction is reversible, and therefore the yield of the various products depends on the acidity (or basicity) of the medium[79,80]. Aldimines are isoelectronic with carbonyl compounds, and can therefore be assumed to react with amines or ammonia in much the same way as carbonyl compounds react with amines:



The use of strongly basic media, such as ammonia, should suppress the formation of Schiff's bases and therefore also the formation of secondary and tertiary amines.

Thus, conditions favourable to the formation of primary amines are obtained by carrying out the reduction of dinitriles in the presence of ammonia, since the tendency to form Schiff's bases is thereby decreased and the reactivity of the aldimines is increased.

V. INFLUENCE OF DINITRILE STRUCTURE ON THE COURSE OF THE REACTION

The course of the catalytic hydrogenation of dinitriles is influenced by the structure of the dinitrile as well as by the experimental conditions and the nature of the catalyst.

Benzonitrile is rapidly reduced on a nickel catalyst at 115–120°, but the naphthonitriles are reduced very slowly, and require an increase in temperature to 180–190° to give a fast reaction[67].

The position of substituents is also important. In the reduction of *o*-, *m*-, and *p*-tolunitriles the yields of primary amines were 61, 54, and 41% respectively; in the case of ω-methoxy-*o*- and ω-methoxy-*p*-tolunitriles they were 44 and 20%; and with 1,2,3,4-tetrahydronaphtho-1-nitrile and -2-nitrile they were[67] 70 and 47%. The activating influence of the phenyl group has been pointed out: under identical conditions, primary amine yields of 21, 36, and 41% were obtained by reduction from phenylpropionitrile, phenylacetonitrile, and benzonitrile respectively.

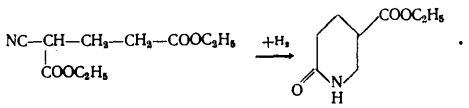
Jadot and Braine[81] showed that benzonitrile is converted into primary and secondary amines on a Raney copper catalyst at 180–200°, whereas phenylacetonitrile is not reduced even when the temperature is raised to 260°.

The effect of nitrile structure on the course of the reaction has been observed also in work on the catalytic reduction of organosilicon nitriles: under identical hydrogenation conditions a higher yield of primary amine is obtained[82] from 3-cyanopropyltriethoxysilane (81%) than from 2-cyanoethyltriethoxysilane (68%). This difference is obviously due to the different positions of the CN groups relative to the silicon atom[83].

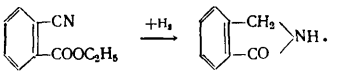
Alkyl groups on the silicon atom have a screening effect in the reduction of *sym*-tetraalkyldi-3-cyanopropyldisiloxanes: the yield of primary amine falls as the alkyl side-chain is made longer. For example, the following compounds, when hydrogenated under identical conditions, gave the corresponding *sym*-tetraalkyldi-4-aminobutyldisiloxanes in yields of 92, 87, and 70% respectively[20]:

$$[NC-(CH_2)_3-Si(CH_3)_2]_2O,$$
$$[NC-(CH_2)_3-Si(CH_3)(C_2H_5)]_2O,$$
$$[NC-(CH_2)_3-Si(C_2H_5)_2]_2O.$$

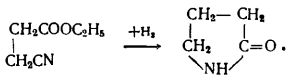
The course of the hydrogenation is particularly sensitive to the nitrile structure when a second reactive group (carbonyl, carboxyl, ethyl carboxylate, hydroxyl, or nitrile) is situated in position 3, 4, or 5 relative to the nitrile group. In this case, cyclisation occurs. There are many examples of this conversion: thus Koelsch[84] obtained ethyl 2-ketopiperidine-5-carboxylate by reducing diethyl α-cyanoglutarate on Raney nickel at 100° under 900 atm hydrogen pressure:



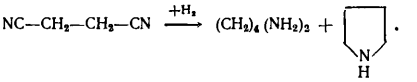
Watanabe[85] observed the formation of a cyclic product, in 73.7% yield, by the reduction of ethyl *o*-cyanobenzoate at 260° on a nickel–copper catalyst supported on silica gel:



Linn[86] obtained 2-pyrrolidone in 91% yield by reducing ethyl β-cyanopropionate on a Raney nickel catalyst at 90° and under an initial hydrogen pressure of 70 atm in an ethanol medium:



By passing the vapour of succinodinitrile in a hydrogen stream over a nickel catalyst at 180–200°, Gaudion[87] observed the formation of small amounts of tetramethylenediamine and pyrrolidine:



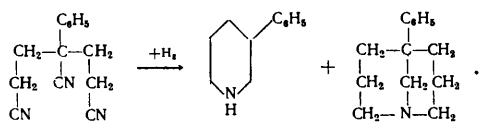
Hydrogenation of succinodinitrile in liquid ammonia on a Raney nickel catalyst at 140° gave pyrrolidine and tetramethylenediamine in 45 and 20% yield respectively[21]. Others[43] obtained pyrrolidine and tetramethylenediamine in 70 and 5% yield respectively by reducing succinodinitrile on Raney nickel at 75°.

It is claimed in a patent[22] that the reduction of glutarodinitrile in the presence of Raney nickel or cobalt on kieselguhr at 172° gives only piperidine (in 83% yield). When the temperature is reduced to 125° in the presence of cobalt on kieselguhr, pentamethylenediamine (41.5% yield) is formed as well as piperidine. Lower yields of piperidine, and the apperance of a diamine among the reaction products, were observed also upon decreasing the reaction time.

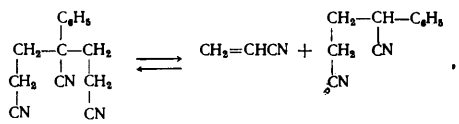
The reduction of glutaronitrile on Raney cobalt in ammonia gave[41] piperidine and pentamethylenediamine in 35 and 55% yield, whereas the primary diamines were obtained in practically quantitative yield from the dinitriles of pimelic,

azelaic, sebacic, and decanedicarboxylic acids. The yield of primary diamines was [41,88] 85–90% in the reduction (on Raney nickel) of the dinitriles of pimelic, azelaic, sebacic, nonanedicarboxylic, decanedicarboxylic, and *trans*-docos--13-enoic acids.

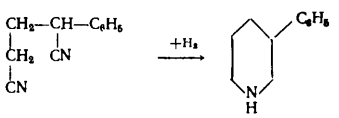
Badger *et al.*[89] hydrogenated 1,3,5-tricyano-3-phenylpentane on copper chromite at 220–230° under an initial hydrogen pressure of 175 atm, and observed the formation of 3-phenylpiperidine (10%) and 5-phenyl-1-azabicyclo-[3,3,1]nonane (15%):



The suggestion has been made[90] that the unstable tricyanide decomposes into vinyl cyanide and a dicyanide:

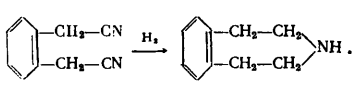


and that 3-phenylpiperidine results from reduction of the dicyanide:

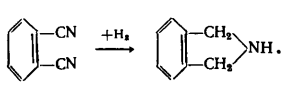


Reduction of the adipodinitrile on Raney nickel or cobalt gives rise to a mixture of the primary diamine and smaller amounts (up to 30%) of secondary diamines, both straight--chain and cyclic.

Catalytic reduction of the dinitriles of *m*- and *p*-phenylenediacetic acids produces high yields of the corresponding primary diamines [10,12,47], whereas the dinitrile of *o*-phenylenediacetic acid gives, as well as the primary diamine, up to 83% of the secondary cyclic amine "benzohexamethyleneimine" [11] [1,2,3,8,9-pentahydrobenzoazepine (Ed. of Translation)]:



The dinitriles of *m*- and *p*-phthalic acids give, respectively, *m*- and *p*-xylylenediamine [13–16,43], but the *o*-phthalodinitrile gives only the cyclic amine (a dihydroisoindole) [43]:



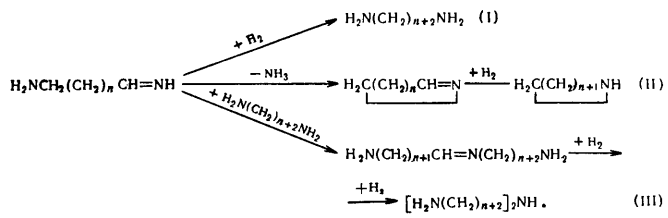
Thus, dinitriles in which the nitrilo-groups are separated by three or four carbon atoms are reduced to a mixture of cyclic and straight-chain amines. Cyclisation is greatly assisted by the presence of two carbon atoms between the CN groups, attached to a benzene ring, in aromatic (or aliphatic–aromatic) *o*-dinitriles.

When there are only two carbon atoms between the nitrilo groups, the formation of an unstrained *N*-heterocycle is favoured, and cyclic products are obtained almost exclusively [43].

Under optimum conditions, the yield of primary diamines from the dinitriles of adipic, glutaric, succinic, and *o*-phthalic acids was 90, 55, 5, and 0% respectively, whilst the cyclic secondary amine was obtained [41] in 5, 35, 70, and 90% yields respectively. Therefore, the tendency of dinitriles to give the cyclic secondary amine during reduction increases in the sequence

adipic < glutaric < succinic < *o*-phthalic.

The structure of the dinitrile appears to influence the course of the reduction by controlling the relative rates of reactions I and II: hydrogenation of the aldimine and intramolecular reaction between the iminomethyl group and the primary amino-group, followed by hydrogenation of the resulting Schiff's base:



With aliphatic α,ω-dinitriles having 7–12 carbon atoms, and also with *m*- and *p*-substituted aromatic dinitriles, hydrogenation of the aldimine is preponderant, and no intramolecular reaction between the iminoethyl and amino--groups takes place. The second reaction (formation of a cyclic amine) predominates in the reduction of dinitriles with two carbon atoms between the nitrilo-groups: neither the use of a selective catalyst (Raney cobalt) nor the use of ammonia as a reaction medium can influence the reaction in the direction of the primary amine [43].

In the intermediate case — reduction of dinitriles with 3–4 carbon atoms separating the nitrilo-groups — we observe a process occurring simultaneously by the reaction paths (I), (II), and (III).

The available data show that the structure of the dinitrile molecule has a profound influence on the course of the reaction.

VI. INFLUENCE OF THE NATURE OF THE CATALYST ON THE COURSE OF THE REACTION

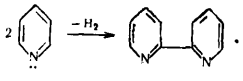
The relative yield of primary and secondary amines in the catalytic reduction of dinitriles depends on the nature of the catalyst as well as on the reaction conditions and on the structure of the dinitrile molecule.

The higher selectivity of Raney cobalt (as compared with Raney nickel) towards formation of primary amines had already been pointed out in work on the catalytic reduction of mononitriles [91,92]. Hydrogenation of aliphatic, aromatic, and organosilicon dinitriles in the presence of a Raney cobalt catalyst invariably gives a higher yield of primary diamines than hydrogenation on Raney nickel [7,8,17,41]. For example, 75–78% of hexamethylenediamine, 10–14% of hexamethyleneimine, and 10–15% of a residue consisting mainly of bishexamethylenetriamine were obtained [41,75] by the reduction of adiponitrile on nickel under the most favourable conditions. On a cobalt catalyst, hexamethylenediamine can be produced in practically quantitative yield, and the cyclic secondary amine amounts to no more than 3–5%. The yield of primary diamines from the dinitriles of pimelic, azelaic, sebacic, and decanedicarboxylic acids reaches 85 and 95% on Raney nickel and Raney cobalt respectively [41].

Cobalt catalysts act more selectively irrespectively of the method of preparation of the catalyst (Raney, boride, supported)[42,56]. Their higher selectivity persists even when the reaction is carried out in the absence of ammonia (*i.e.* under conditions which favour the formation of a secondary amine). Obviously, the selectivity of different metallic catalysts towards the reduction of dinitriles, as well as their activity, is determined mainly by their chemical nature.

Maxted and Walker[93] ascribed the deactivation of metallic catalysts by pyridine and piperidine during hydrogenation to the presence of a free electron pair on the nitrogen atom, which causes these bases to be strongly adsorbed on the catalyst. This view is in agreement with the results of Badger *et al.*[94], who found that the rate of hydrogenation of *trans*-crotonic acid on Raney nickel is significantly decreased by the presence of pyridine and 2,2′-bipyridyl. Pyridine was found to be more "toxic" than 2,2′-bipyridyl.

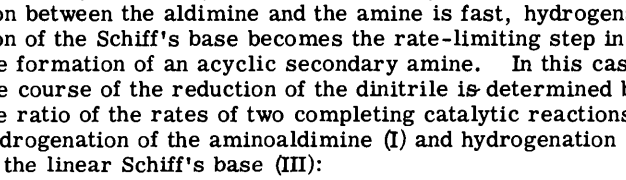
Badger and Sasse[95] obtained heterocyclic biaryls by refluxing monoheterocyclic compounds in the presence of a Raney nickel catalyst; for example, pyridine gave 2,2′-bipyridyl:



The formation of the biaryl indicates that the CH bond in position 3 with respect to the nitrogen atom is activated, probably owing to withdrawal of the electron pair from the nitrogen atom during adsorption of the reacting molecule on the catalyst.

On a Raney cobalt catalyst, on the other hand, no bipyridyl is formed[94], and the rate of hydrogenation of *trans*-crotonic acid is not depressed by the presence of pyridine and 2,2′-bipyridyl.

We have already pointed out that the yield of secondary amines (both cyclic and straight-chain) depends on the relative rate of formation of the Schiff's base and on the rate of its subsequent hydrogenation. The formation of a cyclic Schiff's base is determined almost exclusively by the structure of the dinitrile undergoing hydrogenation, whereas the rate of formation of a linear Schiff's base is largely dependent on the reaction conditions (presence of ammonia, dilution by a solvent, nature of the catalyst). If the reaction between the aldimine and the amine is fast, hydrogenation of the Schiff's base becomes the rate-limiting step in the formation of an acyclic secondary amine. In this case the course of the reduction of the dinitrile is determined by the ratio of the rates of two completing catalytic reactions: hydrogenation of the aminoaldimine (I) and hydrogenation of the linear Schiff's base (III):



The Schiff's base formed during reduction of dinitriles, being an *N*-substituted aldimine, is probably adsorbed on the catalyst less strongly than the unsubstituted aldimine. Therefore, the rate of hydrogenation of the aldimine should be different from the rate of hydrogenation of the Schiff's base. On nickel and cobalt catalysts, the main reduction product of dinitriles with more than 3 carbon atoms separating the CN groups is a primary amine. Hence, we may assume that reaction (I) is faster than reaction (III) on Ni and Co catalysts. From this point of view, the higher selectivity of the cobalt as compared with the nickel catalyst can be ascribed to a greater difference in ease of adsorption between the aldimine and the Schiff's base.

The specificity of the cobalt catalyst cannot manifest itself in the reduction of short-chain dinitriles. When $n = 2$, the tendency of the molecule towards cyclisation is so strong that reaction (II) predominates.

The nature of the catalyst support also can influence the course of the reaction[75].

It may be assumed that all the reacting species in reactions (I), (II), and (III) have activational requirements. To convert an aldimine into a primary amine, the iminomethyl group as well as the hydrogen have to be activated. On the other hand, the conversion of an aldimine into a secondary amine requires activation of two electron-donating (imino- and amino-) groups.

By choosing potential electron acceptors as carriers for the nickel catalyst, we could expect to influence the reduction of nitriles towards the formation of secondary and tertiary amines. Specifically, such a carrier should enhance the adsorption by the catalyst of =NH– and $-NH_2$ groups in the reacting molecules, and should thus affect the relative rates of the competing reactions (I), (II), and (III). In fact, nickel catalysts deposited on acidic (alumina–silica, silica gel, aluminium oxide) or amphoteric carriers (zirconium, titanium, molybdenum, or tungsten oxides) show a marked increase in the formation of secondary and tertiary amines[75].

The appreciable yield of secondary amines from nickel catalysts supported on acidic or amphoteric carriers can also be explained in terms of the very strong adsorption of the unsubstituted aldimine (catalyst poisoning) on the surface of such a catalyst, whilst the more weakly adsorbed Schiff's base is hydrogenated more rapidly.

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SOME ASPECTS OF HIGH-TEMPERATURE CHEMISTRY FROM THE VIEWPOINT OF CHEMICAL THERMODYNAMICS

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I. INTRODUCTION

In the last 10–15 years high-temperature chemistry has begun to develop rapidly into a new branch of chemistry. The concept of high temperature is relative and depends on the range of problems and phenomena considered. Some authors therefore prefer to relate high-temperature chemistry not to definite temperature limits but to various characteristics of the properties of substances and the observed relationships shown by the properties. Thus Brewer[1] defines high-temperature chemistry as the chemistry of systems at sufficiently high temperatures so that the oxidation states, compounds, and general chemical behaviour differ appreciably from those important at room temperature. Searcy[2] defines high temperatures as temperatures at which entropy differences play a major role in determining the position of equilibria of interest (under standard conditions). Using this definition, 3000°K is not a high temperature for the processes of nitrogen ionisation, but for many volatilisation processes, moderately high temperatures or even room temperature (or lower temperatures) could be regarded as high temperatures. There is some justification for this approach, but in the present paper the author prefers, in agreement with Margrave[3], to adopt, albeit arbitrarily, certain definite boundaries on the temperature scale.

In the wide range of temperatures which have now become accessible to a greater or lesser degree (10^{-6}–10^{8} °K), high-temperature chemistry concerns a relatively small interval (of 1–2 orders of magnitude) from about 1000°K to 10000°K (or possibly up to 50000°K), since at higher temperatures almost no molecules remain and atoms undergo increasing ionisation with the formation of plasma. The present paper deals chiefly with the thermodynamic properties of substances at these high temperatures. Other aspects will be touched upon, however, in the discussion of processes of vaporisation.

The marked increase in interest in the physics and chemistry of high temperatures was initially due to the demands made by certain branches of modern technology. This was further stimulated by better availability of high temperatures for experiments, development of methods of study at high temperatures, and the use of fast electronic computers for calculating the thermodynamic functions of various molecules, atoms, and ions at high temperatures using the methods of statistical thermodynamics. Statistical thermodynamics combined with new calculating techniques is widely used in high-temperature chemistry, and it is on this basis that most of the new information on the thermodynamic properties of substances at high temperatures is now obtained, partly because of the great difficulty of making calorimetric determinations even at moderately high temperatures. The methods of statistical thermodynamics are also based on experimental data, but these data are obtained from various types of spectra and by determination of the fundamental parameters of molecular structure (interatomic distances, etc.) by electron and X-ray diffraction studies, etc.

Experimental work in the field of high-temperature chemistry has been accompanied by theoretical work relating to the new experimental methods, methods for calculating thermodynamic properties, and the state of substances at high temperatures. Interest in high-temperature chemistry has also been stimulated by the fact that the previously widely-held views that all chemical relationships became progressively simpler at high temperatures and that there were no fundamentally new problems or phenomena, proved to be greatly oversimplified. The main trends observed on going to very high temperatures are an extremely marked increase in the reactivity of substances, an increase in reaction rates, and the development of processes involving the dissociation and decomposition of complex substances; these are obvious, but at the same time many elements form compounds at high temperatures corresponding to valence states (degrees of oxidation) which are not characteristic, or are unknown for these elements, at ordinary temperatures. Even the relationships between the properties of elements in the same Periodic Group are sometimes found to be more complex than those observed at ordinary temperatures. High temperatures lead to the appearance of species of new types, which may be simpler than the corresponding species at ordinary temperatures (for example CaCl, SiO, Al_2O, AlO, SO) or more complex (C_3, C_9, Na_2, Ge_8, Mg_2, Mo_5O_{15}, $Na_2(OH)Cl$, Ba_2O_3, etc.). At high temperatures, where the thermal motion of the species is capable of breaking chemical bonds, many radicals and free atoms exist in equilibrium with their parent molecules and become essentially molecules themselves. The processes by which they are formed may be quantitatively described by the thermodynamic parameters of the reaction (heat of reaction, entropy change, equilibrium constant, etc.). By determining their temperature dependence, it is often possible, by extrapolation, to obtain interesting conclusions for ordinary temperatures which cannot be arrived at by direct determination at lower temperatures. The tendency for molecules to be simpler at

increased temperatures and the simultaneous increase in the reactivity of atoms lead in particular to the appearance, in a relatively stable state at high temperatures, of diatomic species formed by the most varied combinations of atoms, such as OH, AlO, AlCl, MgCl, MgN, etc., whose existence does not tie up with the ideas on the valence states characteristic of the given elements to which we are accustomed at ordinary temperatures. Atoms of the halogens, oxygen, and hydrogen are able to form diatomic molecules with elements from a wide range of periodic groups (with the exception of the inert gases). At high temperatures, particularly when these are combined with high pressures, it is possible to obtain certain substances in crystalline modifications which cannot be produced at ordinary temperatures or which have been previously unknown (the synthesis of diamonds, cubic crystals of boron nitride, a new crystalline form of SiO_2, etc.).

Information on the change in the chemical and physical properties of elements and their compounds at high temperatures makes it possible to construct, as it were, a temperature axis perpendicular to the plane of the Periodic System and to examine not only the regular features of the properties of the elements and their compounds at ordinary temperatures but also the influence of temperature on these properties and on the relationships between them for different elements. At the present time, of course, high-temperature chemistry is only at the stage of the initial accumulation of material. Many facts revealed experimentally await theoretical explanation. Here the field is wide open for specialists in thermodynamics, statistics, and the theory of chemical bonding and structure. An interesting feature is that some of the fundamental concepts of the Debye–Hückel theory, developed for solutions of strong electrolytes, have been applied successfully to ionised gases.

In recent years there have been a number of international and local conferences [4-8] devoted to various problems in the field of high-temperature chemistry. Many reviews have been published [1-3,9-18]. Various aspects of high-temperature chemistry are now beginning to be more widely reflected in monographs and textbooks [19-25].

Considerable attention is now being paid to methods for attaining high temperatures, methods of measurement, thermal stability of materials and compounds, and their mechanical and other properties at high temperatures. There are a considerable number of papers, however, devoted to the influence of temperature on purely chemical and thermodynamic properties of substances.

The present paper will deal only with the chemical-thermodynamic properties of substances in the gaseous state at constant or varying pressures, and also with the corresponding chemical reactions and processes of vaporisation.

II. GASES AT CONSTANT PRESSURE

The basic equations

$$\Delta G = \Delta H - T\Delta S \qquad (1)$$

$$\Delta G^\circ = -RT \ln K_a \qquad (2)$$

are fully rigorous from the thermodynamic viewpoint and relate the changes in Gibbs free energy ΔG, enthalpy ΔH, and entropy ΔS for a given reaction to one another and to the value of the equilibrium constant K_a at a given temperature of T °K.

The reaction can proceed in the forward direction without the expenditure of work from an external source if $\Delta G < 0$, and the condition for equilibrium is that $\Delta G = 0$. Thus reaction in the direction indicated is favoured by high negative values of ΔH (*i.e.* considerable liberation of energy) and high positive values of ΔS (*i.e.* increase in the entropy of the system). For many reactions which are not too complex, the first (energetic) factor reflects the usual increase in the stability of a system with decrease in its reserve of internal energy, manifested in a tendency towards greater aggregation of the substance, increase in the size of the species, etc., whereas the second (entropy) factor reflects the tendency towards intensification of all processes involving dissociation to simpler species under the influence of the thermal motion of the species [26]. In reactions which bring the system towards an equilibrium state, these two factors operate in opposite directions, and the overall course of the reaction is determined by the influence of whichever factor predominates until the influences of the two factors become equal, when the equilibrium state is reached. Since the heat of reaction ΔH usually depends little on the concentrations of the reactants, the attainment of equilibrium is almost entirely governed by the dependence of the entropy on concentration [27].

Eqns. (1) and (2) show that, other conditions being equal, the relative importance of the entropy factor increases with increase in temperature. Under standard conditions at low temperatures, the term $T\Delta S^\circ$ is small since the values of T are small, but at high temperatures this term shows a corresponding increase. For many types of gas reactions, ΔH° and ΔS° change relatively slowly with temperature, particularly when compared with the change in T, so that in these cases $T\Delta S^\circ$, and hence ΔG°, can often be roughly thought of as linear functions of temperature. In these cases $\ln K$ is a linear function of the reciprocal of the temperature $(1/T)$. Fig. 1 shows the relationships between these quantities for the thermal dissociation of I_2 to free atoms. For this reaction under standard conditions, the influence of the energy factor predominates up to 1455 °K and that of the entropy factor above 1455 °K. At T = 1455 °K the influences under standard conditions are of equal magnitude but opposite sign. At this temperature $\Delta G^\circ = 0$, so that $\ln K_a = 0$ and $K_a = 1$. At the same temperature but with concentrations of the components different from the standard values, ΔG differs from zero and may be either positive or negative, depending on the ratio of the concentrations and hence on the value of ΔS. Independently of this, however, at T = 1455 °K for this reaction $\ln K_a = 0$ and $K = 1$. At this temperature the dissociation process

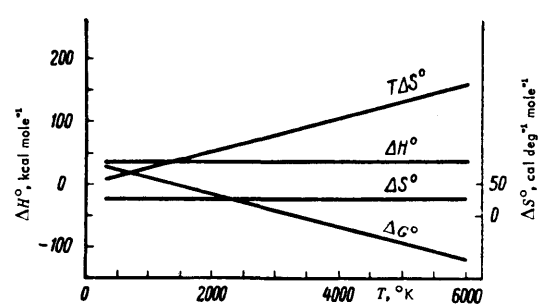

Fig. 1. Thermodynamic parameters of the reaction $I_2 \rightleftharpoons 2I$ at temperatures up to 6000 °K.

undergoes a steep change. Dissociation begins at much lower temperatures and increases with increase in temperature to 1455°K and above. At this temperature the equilibrium constant passes through a value equal to unity, which for this reaction at p = 1 atm corresponds to a degree of dissociation x = 0.447 (and to corresponding different values of x for other pressures).

The most characteristic distinguishing feature of the influence of high temperatures at constant pressure is an increase in the rates of decomposition, dissociation, and disaggregation, associated with the increased importance of the entropy factor reflecting the influence of the thermal motion of the species.

As a result, the processes which become typical are those involving a decrease in the number of atoms per molecule, often associated with a change in the valence state (degree of oxidation) of the element, with further decomposition of the molecule to free atoms and then successive removal of the least firmly held electrons from the atoms to yield a plasma. It should be emphasised that this thermal ionisation of atoms, unlike ionisation under the influence of light and high-energy species, is characterised by a definite equilibrium state whose position depends on temperature and pressure. It is described by the usual thermodynamic relationships and, in particular, can be calculated by the methods of statistical thermodynamics.

A characteristic example of the influence of increase in temperature is provided by the sequence of changes:

$$MgCl_2 \longrightarrow MgCl \longrightarrow Mg \longrightarrow Mg^+ \longrightarrow Mg^{2+},$$

corresponding, for example, to the successive processes

$$MgCl_2 \rightleftharpoons MgCl + Cl, \quad (a)$$

$$MgCl \rightleftharpoons Mg + Cl, \quad (b)$$

$$Mg \rightleftharpoons Mg^+ + e, \quad (c)$$

$$Mg^+ \rightleftharpoons Mg^{2+} + e. \quad (d)$$

Fig. 2 shows the change in the degree of dissociation x with change in temperature for the first two reactions, for the particular case where the total pressure P is equal to 1 atm. The calculation was carried out from the values of K recommended [28] for the reactions

$$MgCl_2 \rightleftharpoons Mg + 2Cl \text{ and } MgCl \rightleftharpoons Mg + Cl,$$

assuming

$$x = \sqrt{\frac{K_P}{K_P + P}}.$$

The correspoinding values of x for the process of ionisation to Mg^+ were calculated by a similar conventional method.

The increase in the part played by the entropy factor leads to simpler relationships between the corresponding parameters for reactions and processes of the same type (see below), since for these we observe smaller differences in ΔS_T°, similar changes in ΔS° with temperature, etc. [29-31]. Table 1 gives the chief thermodynamic quantities for the dissociation of diatomic molecules of the alkali metals and halogens from published data [32,33].

The more atoms in the original molecule, the greater the variety of different species in the dissociation products and, correspondingly, the complexity of the relationships between the composition of the dissociation products at different temperatures. The compositions of the dissociation products of H_2O and CO_2 at different temperatures are shown in Figs. 3 and 4. Fig. 3 is based on calculations [34] in which allowance was made for the concentration of the following species: H_2O, OH, H_2, O_2, H, and O. The composition of the products of the thermal dissociation of H_2O in this case is expressed in terms of the concentration of these

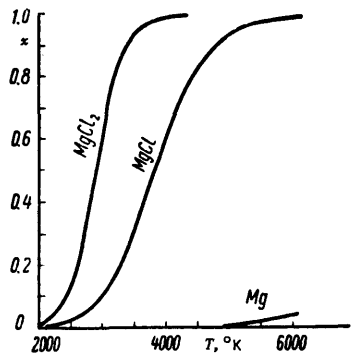

Fig. 2. Temperature dependence of the degree of dissociation of magnesium dichloride and monochloride according to reactions (a) and (b) and of the ionisation of magnesium atoms according to reaction (c).

TABLE 1. Basic thermodynamic parameters for the dissociation of the diatomic molecules of the alkali metals and of the halogens at 298.15°K (ΔH° kcal mole^{-1}, ΔS° cal deg^{-1} × × mole^{-1}).

Substance	ΔS°_{298}	ΔH°_{298}	$\log K_d$	$\Delta S^\circ_{1800} - \Delta S^\circ_{298}$
Li_2	−19.29	26.41	−15.16	−1.42
Na_2	−18.43	18.00	− 9.17	−1.20
K_2	−16.93	12.26	− 5.29	−1.02
Rb_2	−16.56	11.65	− 4.92	−1.09
Cs_2	−16.08	10.71	− 4.35	−0.91
F_2	−27.35	37.81	−21.72	−3.21
Cl_2	−25.63	57.88	−36.63	−3.15
Br_2	−24.97	53.52	−28.88	−1.91
I_2	−24.08	50.96	−24.58	−1.55

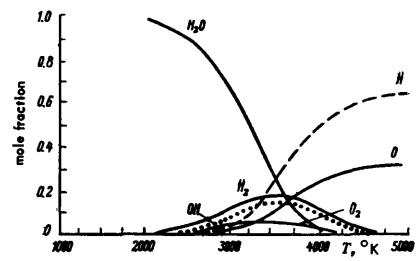

Fig. 3. Relative concentration (in mole fractions) of various species (OH, H_2, O_2, H, and O) in the products of the thermal dissociation of water vapour at various temperatures.

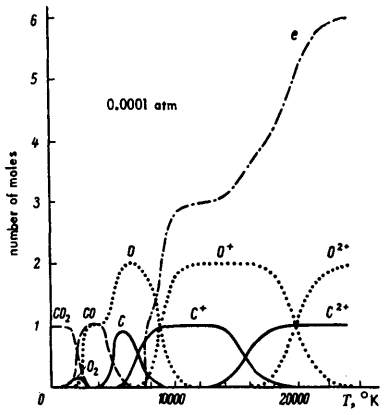

Fig.4. Concentration of various species (CO, C, O_2, O, C^+, C^{2+}, O^+, and O^{2+}) in the products of the thermal dissociation of CO_2 at $P = 0.0001$ atm, expressed as the number of moles of each species formed from 1 mole of CO_2.

species (in mole fractions) for a total pressure $P = 1$ atm. (Data for other pressures were also published[34].) For the same system, other authors[35,36] carried out calculations covering higher temperatures, at which ionisation of hydrogen and oxygen atoms and hydroxyl radicals occurs. An interesting feature is that in this system, at temperatures in the region of 4000°K (at $P = 1$ atm) (Fig. 2), the concentration of free hydroxyl radicals OH in the mixture is higher than the concentration of H_2O molecules. This is due to the fact that removal of the second hydrogen atom requires a slightly greater expenditure of energy than removal of the first.

Fig. 4 gives the product composition for the thermal dissociation of CO_2 at different temperatures ($P = 10^{-4}$ atm), expressed as the number of moles (or gramme-atoms or gramme-ions) of species of different type obtained from one mole of the original CO_2.[37] Here the calculation was carried out up to 24 000°K, *i.e.* it covers the range of the first and second ionisations of oxygen and carbon atoms at this pressure, but no allowance was made for the formation of carbon suboxide C_3O_2 or for the polymerisation of carbon vapour, *i.e.* the formation of C_2, C_3, etc. molecules. Data for other pressures up to $P = 100$ atm were also published[37]. The calculation was carried out in connection with a study of the possible state of the atmosphere of Venus.

Various data relating to the thermodynamic functions of substances in the gaseous state have also been given for a number of other systems such as the ionisation of alkali metal vapours[38], etc.[39-43].

The values of the main thermodynamic functions for the gaseous state under standard conditions at high temperatures have now been calculated for a large number of substances with molecules of the simplest type. Most of these calculations have been carried out for diatomic molecules of the type AB (the monoxides, monohalides, and monosulphides of various elements), many of them simply on the basis of the corresponding molecular constants in the rigid rotator–harmonic oscillator approximation, *i.e.* with the assumption that the rotation of the molecule can be regarded as the rotation of a completely rigid system and that the anharmonicity of the vibrations can be neglected. This assumption restricts appreciably the applicability of this method of calculation for temperatures above 1500–2000°K, since for many substances the results are appreciably different when allowance is made for the anharmonicity of the vibrations, let alone that for excited states (excitation of atoms and electronic excitations) which requires appropriate data on the spectra of the molecules and other methods of calculation.

For most elements in the monatomic-gas state and also for many elements in the state of diatomic or more complex molecules, the main thermodynamic functions and the thermodynamic parameters of the reactions of their formation from the ordinary simple elements for temperatures up to 3000°K have been tabulated[32]. Data have been given[40] on the high-temperature components of the enthalpy and entropy up to 5000–8000°K for many elements in the monatomic-gas state and for certain diatomic molecules. The main thermodynamic functions for the monatomic-gas state have been calculated for most elements up to 8000°K[44-48] and also for positive ions (singly-, doubly-, triply-, and quadruply-charged) up to 50 000°K.[49] The experimental basis for all this work is provided by appropriate spectroscopic data taken for the most part from reference tables[50]. It has become possible to carry out these complex and tedious calculations on a large scale through the use of electronic computers.

Table 2 gives as an example the values of the function $(H_T^\circ - H_0^\circ)/T$ for the singly-charged positive ions of certain elements at different temperatures up to 50 000°K.[49] For monatomic species the specific heat and internal energy do not have vibrational and rotational components and are determined entirely by the translational movement of the species and (at higher temperatures) by the excitation of higher electronic energy levels. Before these excitations take place, the specific heat C_P° and the function $(H_T^\circ - H_0^\circ)/T$ have a constant value of 4.9682 cal deg^{-1} mole^{-1} for species of a given type. In this series of species the change from the structure of He atoms to those of Ne, Ar, Kr, Xe, and Rn is accompanied by a lowering of the first excited electronic state from 21.0 eV for helium atoms to 6.8 eV for radon atoms[50]. The influence of excited states does not yet manifest itself at 45 000°K for Li^+ ions, 20 000°K for Na^+ ions, 10 000°K for K^+ and Rb^+ ions, and 9000°K for Cs^+ ions. Similar relationships should also hold for F^-, Cl^-, Br^-, and I^- ions and for Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} ions, etc.; for isoelectronic species, increase in the charge on the nucleus is also associated with a rise of the first excited electronic state and hence with an increase in the temperature at which it begins to influence the thermodynamic functions.

TABLE 2. Enthalpy function $(H_T^\circ - H_0^\circ)/T$ for the singly-charged ions of certain elements at high temperatures (cal × × deg^{-1} g-atom^{-1}).[49]

T, °K	Ne^+	Li^+	Na^+	C^{2+}	Mg^+	Ba^+	Al^+	Tl^+
298.15	5.0533	4.9682	4.9682	4.9682	4.9682	4.9682	4.9682	4.9682
2000	5.2160	4.9682	4.9682	4.9682	4.9682	5.7143	4.9682	4.9682
4000	5.1213	4.9682	4.9682	4.9682	4.9684	6.5849	4.9685	4.9682
6000	5.0774	4.9682	4.9682	4.9682	4.9779	6.5090	4.9881	4.9686
8000	5.0528	4.9682	4.9682	4.9682	5.0334	6.3795	5.1098	4.9769
10 000	5.0372	4.9682	4.9682	4.9684	5.1503	6.3406	5.3983	5.0170
20 000	5.0041	4.9682	4.9682	5.4013	6.9102	7.7444	7.9331	6.4657
30 000	4.9972	4.9682	4.9700	8.8021	9.6147	8.6237	11.320	9.6355
40 000	5.0614	4.9682	5.0138	11.383	10.281	8.4389	12.312	11.182
50 000	5.3676	4.9689	5.2807	11.531	9.9249	8.0438	11.767	11.100

The values of C_P° and $(H_T^\circ - H_0^\circ)/T$ mentioned above are likely to stay unchanged with increase in temperature for the longest time for species with an eight-electron shell in the outer layer (Ne, Ar, Kr, Xe, and Rn atoms and the isoelectronic Na^+, K^+, Rb^+, and Cs^+ ions), followed by species containing only *s* electrons in the outer layer (Be, Mg, Ca, Sr, and Ba atoms and the isoelectronic B^+ and Al^+ ions, but not Sc^+, Y^+, or La^+).

Fig. 5 shows the temperature dependence of specific heat C_P° for certain gases with monatomic and diatomic molecules up to 6000°K. For atoms which are difficult to excite and for ions with similar electronic structures, C_P° throughout the whole of this temperature range retains its constant (minimum) value of 4.97 cal deg^{-1} mole^{-1} corresponding to the specific heat of translational motion. Halogen atoms have a slightly higher specific heat, that of bromine passing through an indistinct maximum at about 2000°K, while that of iodine increases appreciably in the range 2000–4000°K, after which it remains almost constant up to 6000°K. It can readily be seen that Li, Na, K, and Cs differ sharply from the halogens and make up a group with a similar temperature dependence of C_P°, but appreciably different position of the C_P° curves. Atoms with different structures (Mg, Fe, Pb) show a different type of relationship. All this shows that the change in the specific heat C_P°, and hence in S_T°, $H_T^\circ - H_0^\circ$ and other thermodynamic functions with change in temperature is not completely smooth or, more precisely, the derivatives of these quantities with respect to temperature are not monotonic. This of course applies not only to very high temperatures. The introduction of new degrees of freedom (in particular, new vibrational levels in polyatomic molecules) produces a similar effect, albeit generally less marked, even at moderately high temperatures. The widely-used methods of expressing thermodynamic functions in analytical form in power series with respect to absolute temperature in many cases leads to excessive smoothing out of significant variations. This is true not only of thermodynamic functions. Fig. 6 shows the change in the number of species in 1 cm^3 of the products of the thermal dissociation of CO_2 with change in temperature at constant pressure.

Accumulation of multiplicity of data on the thermodynamic properties of species (atoms, ions, and molecules) is not necessarily accompanied by a corresponding increase in information on the parameters of the reactions between them: only the entropy change for the reaction can be calculated from the values of the entropies of its components.

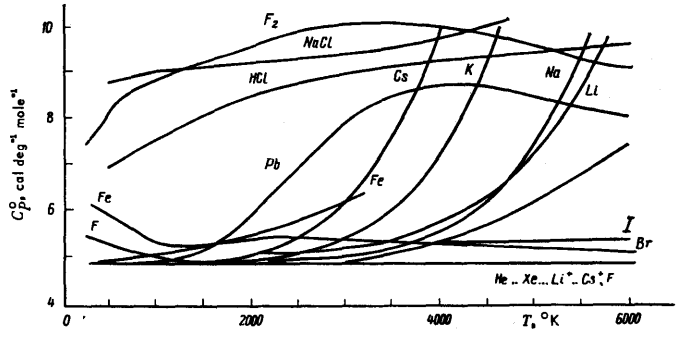

Fig.5. Temperature dependence of the specific heat C_P° for certain substances in the ideal-gas state.

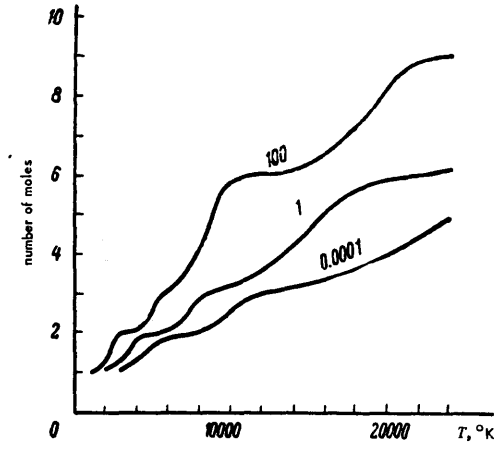

Fig.6. Temperature dependence of the total number of species per unit volume in the products of the thermal dissociation of CO_2 at pressures of 100, 1, and 0.0001 atm, expressed as the number of moles in 1 cm^3 (reduced to normal conditions).

In order to determine the corresponding enthalpy change ΔH, Gibbs free energy change ΔG, equilibrium constant K_a, and other related quantities, a knowledge of the heat of reaction or equilibrium state for at least one temperature is necessary. The methods of statistical thermodynamics cannot yet be used for this purpose. The value of ΔH for the formation of the simplest molecules from the free atoms can in many cases be calculated from the dissociation energy determined from spectroscopic data. For this, the ground states adopted in calculations from spectroscopic and thermochemical data must be identical, but this has not always been the case in the past.

Mass-spectrometric determinations on vapours at different temperatures are now beginning to provide a new source of information on thermodynamic parameters (see below).

III. THERMODYNAMIC DETERMINATIONS BASED ON THE CHEMICAL SIMILARITY OF SUBSTANCES AND REACTIONS

Much of the new information on the thermodynamic properties of different substances and the thermodynamic parameters of reactions has come from the use of the chemical similarity between substances on the basis of various methods of comparative calculation. The rapid increase in the demand for thermodynamic data as a result of the extension of the range of substances acquiring practical importance and the tedious and often time-consuming nature of the experimental determination of some of these quantities have stimulated the development of methods of comparative calculation. By making use of the analogy in the chemical properties of appropriate substances, it is possible by these methods to estimate the thermodynamic properties of the required substances and the reaction parameters on the basis of experimental data for other substances and reactions chemically similar to the first.

Thus the method of related compounds and reactions is based on a comparison of the analogous compounds of elements in the same subgroup of the Periodic System, present in these compounds in the same valence (oxidation) state and showing a sufficiently complete analogy between one another in this state. Such related compounds as, for example, the alkaline earth metal carbonates have values of the chief thermodynamic functions which are related to one another in regular fashion; their temperature dependences do not usually differ markedly and any difference is regular. Different degrees of related character can be considered. Thus the compounds of lithium, beryllium, and to some extent boron, are not infrequently less similar to the corresponding compounds of their analogues than the latter are to one another. This is apparently due to the absence from their ions of the eight-electron shell present in the ions of their higher analogues. A two-row difference is less favourable than a one-row difference, and in the case of a three-row difference the method generally cannot be recommended. The conditions are also unfavourable if the differing atoms predominate with respect to mass or dimensions in the molecule, as in the hydrogen halides, for example.

Without dealing at this stage with the reasons for the simpler relationships between thermodynamic properties for substances of the same type, we would merely point out that internal structures of the same type entail in the first place simpler relationships between the values of the entropy, the entropy changes in reactions of the same type (see below), and their temperature dependence, since the magnitude of the entropy is sensitive to all the characteristic features of the internal structure of substances. At the same time, in the high-temperature range, the methods of comparative calculation are often particularly valuable because calculations by the methods of statistical thermodynamics become more complex and experimental determinations more difficult. It is therefore necessary to get to know the extent and the temperature limits to which the various methods of comparative calculation (established for the most part for ordinary or moderately high temperatures) remain applicable at high temperatures, and what restricts their applicability under these conditions.

For the ideal-gas state, the changes in the high-temperature components of the entropy ($S^\circ_T - S^\circ_{T_1}$) with change in temperature for substances of strictly the same type should be related to one another in regular fashion [29-31,51,52]. For the most part the ratio of, or the difference between, these changes for two substances of the same type X and Y

$$\frac{(S^\circ_T - S^\circ_{T_1})_Y}{(S^\circ_T - S^\circ_{T_1})_X} = \alpha_S \qquad (3)$$

or

$$(S^\circ_T - S^\circ_{T_1})_Y - (S^\circ_T - S^\circ_{T_1})_X = c \qquad (4)$$

can be regarded as approximately constant quantities over a more or less extensive temperature range. Similar expressions also relate the high-temperature components of the enthalpy [51,53,54]

$$\frac{(H^\circ_T - H^\circ_{T_1})_Y}{(H^\circ_T - H^\circ_{T_1})_X} = \alpha_H \qquad (5)$$

or

$$(H^\circ_T - H^\circ_{T_1})_Y - (H^\circ_T - H^\circ_{T_1})_X = a. \qquad (6)$$

It is convenient to take as temperature T_1 the value 298.15°K = 25°C, from which the values of the high-temperature components of the thermodynamic functions are given in reference literature [40]. The use of slightly higher temperatures for this purpose, however, sometimes improves the applicability of relationships (3)–(6). For substances of sufficiently similar type, the high-temperature components of the entropy at a given temperature are for the most part similar to one another, so that for such substances Eqns. (3) and (4) apply approximately and simultaneously. The same is true of Eqns. (5) and (6).

In the most favourable cases the various equations (3)–(6) apply also in the low-temperature range, so that it is then possible to take 0°K as the temperature T_1 without introducing any appreciable errors. Comparison of the quantities $S^\circ_T - S^\circ_{298}$ and $H^\circ_T - H^\circ_{298}$ has the advantage over comparison of the quantities S°_T and $H^\circ_T - H^\circ_0$ in that the low-temperature values of the enthalpy and entropy need not be known.

Table 3 gives the values of S°_T for sodium and potassium fluorides and chlorides in the ideal-gas state under standard conditions at different temperatures up to 6000°K from published data [28]. These four substances suitably paired exhibit fairly rigorous common-type character. For these substances, throughout the whole of this temperature range, the ratios α and differences c remain fairly constant. When compared with sodium or potassium fluorides and chlorides, however, the analogous lithium compounds show a more marked variation in the values of α and c with change in temperature.

Similar relationships are observed for the enthalpies of lithium, sodium, and potassium halides. The temperature dependences of the quantities

$$\alpha_H = \frac{(H^\circ_T - H^\circ_0)_Y}{(H^\circ_T - H^\circ_0)_X}$$

and

$$a = (H^\circ_T - H^\circ_0)_Y - (H^\circ_T - H^\circ_0)_X$$

are slightly more marked than those for α_S and c.

These relationships make it possible to calculate otherwise unavailable data sufficiently reliably by this method of comparison. Thus by using the values of S°_T for sodium chloride at different temperatures it is possible to calculate S°_T for potassium chloride at high temperatures (with an accuracy of up to ±0.5 e.u. up to 6000°K) if the values of S°_T for these compounds at some single temperature are known.

The double-comparison method (see below) makes the last condition superfluous. Comparison of compounds with different anions (particularly complex anions) usually gives somewhat worse results than comparison of compounds in which only the cations differ.

TABLE 3. Values of the entropy S°_T (cal deg^{-1} mole^{-1}) of the gaseous fluorides and chlorides of sodium and potassium [28] and the ratio between them at various temperatures.

T, °K	S°_T				α			c	
	NaF	NaCl	KF	KCl	$\frac{NaCl}{NaF}$	$\frac{KCl}{KF}$	$\frac{KF}{NaF}$	NaCl—NaF	KF—NaF
298.15	51.872	54.882	54.079	57.102	1.059	1.056	1.043	3.01	2 21
1000	62.289	65.587	64.610	67.920	1.052	1.051	1.037	3.30	2.32
2000	68.454	71.920	70.785	74.332	1.051	1.050	1.034	3.47	2.33
3000	72.073	75.714	74.407	78.226	1.051	1.051	1.032	3.64	2.33
4000	74.643	78.487	76.978	81.143	1.052	1.054	1.031	3.84	2.34
5000	76.638	80.726	78.972	83.488	1.053	1.057	1.030	4.09	2.33
6000	78.268	82.639	80.603	85.414	1.056	1.060	1.030	4.37	2.34

An important factor limiting the applicability of these relationships at high temperatures is the thermal excitation of new vibrational or electronic energy levels, since this often takes place at temperatures which differ appreciably even for molecules, atoms, or ions of the same type (see Fig. 5). In this respect the most stable species at high temperatures are naturally atoms and ions which in the free state or in the given state have a closed electron shell like that of the inert gas atoms. These include the Li^+, Na^+, K^+, F^-, and Cl^- ions making up the above halides of lithium, sodium, and potassium.

Comparison of beryllium and magnesium monofluorides and monochlorides gives equally good results, up to 4000–5000°K at least, since the influence of excited states in the Be^+ and Mg^+ ions manifests itself only from 4000°K (see Table 2). In the comparison of S°_T for the nitrides of boron and aluminium BN(gas) and AlN(gas), the ratio α_S varies from 1.07 to 1.05 and the difference c from 3.86 to 3.41 (for values of S°_T from 54 e.u. to 80 e.u.); as for $H^\circ_T - H^\circ_0$ for these substances, the difference a up to 5000°K amounts up to 0.65 kcal mole^{-1}, but at 6000°K it reaches 1.4 kcal mole^{-1} (for values of $H^\circ_T - H^\circ_0$ from 2 kcal mole^{-1} to 53 kcal mole^{-1}).

When insufficient data are available for compounds which are strictly of the same type as the compounds for which information is required, it is sometimes necessary in practice to compare substances which are less similar, for example, the compounds of lithium, beryllium, and to some extent boron, mentioned above, or the analogous compounds of elements belonging to a different group or subgroup of the Periodic System, or the first members of a homologous series of organic compounds, or substances which are less rigorously of the same type for other reasons. In such cases good results are given by the double-comparison method[56], which requires a large number of initial data for the calculation, but which makes it possible to obtain more accurate results than from the comparison of compounds which are less rigorously of the same type. The method is based on the introduction into the calculation of another pair of compounds analogous to those under consideration and the assumption that the temperature dependence of the quantities α or c is the same for both these pairs of compounds. As an example, for four such compounds of the type AX, BX, AY, and BY (say lithium and sodium fluorides and chlorides), it may be assumed that the ratio

$$\frac{(S^\circ_T - S^\circ_{T_1})_{AX}}{(S^\circ_T - S^\circ_{T_1})_{BX}} : \frac{(S^\circ_T - S^\circ_{T_1})_{AY}}{(S^\circ_T - S^\circ_{T_1})_{BY}} = \frac{\alpha_X}{\alpha_Y} \quad (7)$$

and the difference

$$[(S^\circ_T - S^\circ_{T_1})_{AX} - (S^\circ_T - S^\circ_{T_1})_{BX}] - [(S^\circ_T - S^\circ_{T_1})_{AY} - (S^\circ_T - S^\circ_{T_1})_{BY}] = c_X - c_Y \quad (8)$$

do not change with temperature.

In practice it is often sufficient to assume that $\frac{\alpha_X}{\alpha_Y} = 1$ or that $c_X - c_Y = 0$, *i.e.* that

$$\frac{(S^\circ_T - S^\circ_{T_1})_{AX}}{(S^\circ_T - S^\circ_{T_1})_{BX}} = \frac{(S^\circ_T - S^\circ_{T_1})_{AY}}{(S^\circ_T - S^\circ_{T_1})_{BY}} \quad (9)$$

and

$$(S^\circ_T - S^\circ_{T_1})_{AX} - (S^\circ_T - S^\circ_{T_1})_{BX} = (S^\circ_T - S^\circ_{T_1})_{AY} - (S^\circ_T - S^\circ_{T_1})_{BY}. \quad (10)$$

Similar equalities have also been given for the enthalpy[55]. All these relationships can be used, for example, for compounds of elements in two different (preferably adjacent) groups of the Periodic System, with analogous formulae. Thus Table 4 gives the values of α and c for the monochlorides of sodium and lithium, magnesium and beryllium, *i.e.* normal molecules and species which in a certain temperature range exhibit unsaturated valency (radicals). Despite these severe comparison conditions, each of the quantities α and c remains fairly constant up to 6000°K, and this makes it possible, for each pair of substances, to determine unavailable values of S°_T with an accuracy of ~ 1.5% using α for the calculations, or of 1 e.u. using c, taking only one value at some temperature for the required substance. At the same time, for each temperature, the values of all three quantities α (and all three quantities c) are close to one another and change in approximately parallel fashion with change in temperature. The ratio of the two given quantities α_1/α_2 and the difference between the two given quantities $c_1 - c_2$ thus show even smaller changes with change in temperature, and this may be made the basis of calculations of higher accuracy (up to 0.3% in calculations using α_1/α_2 and up to 0.35 e.u. in calculations using $c_1 - c_2$). Moreover, all the ratios of the values of α differ little from unity and all the differences in the values of c differ little from zero. Thus when there are no data on S°_T for the required substance (for any temperature), it is possible to assume that α_1/α_2 equals unity or that $c_1 - c_2$ equals zero, and to calculate its S°_T values at different temperatures with an accuracy of up to 0.7% for calculations using α_1/α_2 and up to 0.5 e.u. for calculations using $c_1 - c_2$. This example is not the best, but in many cases the attainable accuracy will of course be less.

TABLE 4. Ratio between the values of the entropy S°_T of the monochlorides of sodium and lithium, magnesium and beryllium, and aluminium and boron, at various temperatures.[28]

T, °K	$\frac{\alpha_1}{NaCl}$ / $\frac{}{LiCl}$	$\frac{\alpha_2}{MgCl}$ / $\frac{}{BeCl}$	$\frac{\alpha_3}{AlCl}$ / $\frac{}{BCl}$	α_1/α_2	c_1 NaCl—LiCl	c_2 MgCl—BeCl	c_3 AlCl—BCl	$c_1 - c_2$
298.15	1.080	1.073	1.069	1.0070	4.08	3.78	3.52	0.30
1000	1.074	1.070	1.066	1.0037	4.50	4.31	4.04	0.19
2000	1.068	1.064	1.062	1.0036	4.60	4.39	4.13	0.21
3000	1.066	1.062	1.059	1.0035	4.68	4.48	4.19	0.23
4000	1.065	1.060	1.058	1.0046	4.79	4.47	4.26	0.32
5000	1.065	1.059	1.057	1.0056	4.92	4.51	4.32	0.41
6000	1.066	1.058	1.057	1.0070	5.09	4.55	4.43	0.54

Similar relationships exist for the enthalpy, but here the discrepancies are greater. Table 5 gives an example of the calculation of the enthalpy $H^\circ_T - H^\circ_0$ for magnesium monochloride from the data for gaseous lithium, sodium, and beryllium monochlorides using the two equations

$$(H^\circ_T - H^\circ_0)_{MgCl} = \frac{(H^\circ_T - H^\circ_0)_{NaCl}}{(H^\circ_T - H^\circ_0)_{LiCl}} (H^\circ_T - H^\circ_0)_{BeCl} \quad (11)$$

and

$$(H^\circ_T - H^\circ_0)_{MgCl} = (H^\circ_T - H^\circ_0)_{NaCl} - (H^\circ_T - H^\circ_0)_{LiCl} + (H^\circ_T - H^\circ_0)_{BeCl}. \quad (12)$$

The calculated values begin to deviate appreciably from the published data at temperatures above 3000°K.

Table 6 gives the high-temperature component of the entropy ($S^\circ_T - S^\circ_{298}$) for MgCl calculated from the equations

$$(S^\circ_T - S^\circ_{298})_{MgCl} = \frac{(S^\circ_T - S^\circ_{298})_{NaCl}}{(S^\circ_T - S^\circ_{298})_{LiCl}} (S^\circ_T - S^\circ_{298})_{BeCl} \quad (13)$$

$$(S^\circ_T - S^\circ_{298})_{MgCl} = (S^\circ_T - S^\circ_{298})_{NaCl} - (S^\circ_T - S^\circ_{298})_{LiCl} + (S^\circ_T - S^\circ_{298})_{BeCl}. \quad (14)$$

With the exception of the entropy at 6000°K, the deviations between the calculated and published values do not exceed 0.12 e.u.

TABLE 5. Enthalpy ($H_T^\circ - H_0^\circ$) of the gaseous monochlorides of lithium, sodium, beryllium, and magnesium (kcal mole^{-1}) from published data[28] and ($H_T^\circ - H_0^\circ$) for magnesium monochloride, calculated from Eqns. (11) and (12).

T, °K	$H_T^\circ - H_0^\circ$			$(H_T^\circ - H_0^\circ)$ MgCl				
	LiCl	NaCl	BeCl	published data	from Eqn. (11)	Δ	from Eqn. (12)	Δ
298.15	2.16	2.30	2.12	2.23	2.26	+0.03	2.26	+0.03
1000	8.19	8.54	8.00	8.38	8.34	−0.04	8.35	−0.03
2000	17.19	17.69	16.89	17.38	17.38	0.00	17.39	+0.01
3000	26.35	27.05	25.91	26.50	26.60	+0.10	26.61	+0.11
4000	36.64	36.70	35.04	35.77	36.08	+0.31	36.10	+0.33
5000	45.06	46.74	44.33	45.25	45.98	+0.73	46.01	+0.76
6000	54.65	57.23	53.84	54.98	56.38	+1.40	56.42	+1.44

TABLE 6. High-temperature components of the entropy ($S_T^\circ - S_{298}^\circ$) of the gaseous monochlorides of lithium, sodium, beryllium, and magnesium (cal deg^{-1} mole^{-1}) from published data[28] and ($S_T^\circ - S_{298}^\circ$) for magnesium monochloride, calculated from Eqns. (13) and (14).

T, °K	$S_T^\circ - S_{298}^\circ$			$(S_T^\circ - S_{298}^\circ)$ MgCl				
	LiCl	NaCl	BeCl	published data	from Eqn. (13)	Δ	from Eqn. (14)	Δ
1000	10.28	10.71	9.99	10.53	10.41	−0.12	10.42	−0.11
2000	16.52	17.04	16.15	16.76	16.66	−0.10	16.67	−0.09
3000	20.23	20.83	19.78	20.46	20.37	−0.09	20.38	−0.08
4000	22.90	23.61	22.43	23.12	23.13	+0.01	23.14	+0.02
5000	25.00	25.84	24.50	25.24	25.32	+0.08	27.34	+0.10
6000	26.75	27.86	26.24	27.01	27.32	+0.31	27.35	+0.34

In a similar comparison of S_T° for the gaseous trifluorides of nitrogen and phosphorus NF_3 and PF_3 with the radicals CF_3 and SiF_3, the quantity α_1/α_2 changes from 0.007 to 0.011 [presumably 1.007 to 1.011 (Ed. of Translation)] and $c_1 - c_2$ changes from 0.49 to 1.1 e.u., that is, when Eqns. (9) and (10) are used, in which $T_1 = 0$°K, the possible error does not exceed about 1.1 e.u. for an absolute value of S_T° up to 120 e.u.; for $S_T^\circ - S_{298}^\circ$ it decreases to 0.6 e.u. In the calculation of $H_T^\circ - H_0^\circ$ the error amounts to not more than 0.5 kcal mole^{-1} for an absolute value of $H_T^\circ - H_0^\circ$ of 113 kcal mole^{-1}.

Chemical *reactions* of the same type, *i.e.* analogous changes in compounds of the same type (with identical stoichiometric coefficients in the reaction equations), show simple relationships between the corresponding thermodynamic parameters at the same temperature or under other comparable conditions. The temperature dependences of the thermodynamic parameters of reactions of the same type are as a rule even closer. With increase in temperature the influence of the entropy factor $T\Delta S^\circ$ on the position of equilibrium becomes more pronounced. As a result, the simpler relationships observed for it in reactions of the same type make this method of common-type reactions particularly fruitful in the examination of various thermodynamic relationships in the high-temperature range.

One characteristic feature of reactions of the same type is that the standard entropy changes ΔS° in the reactions at the same temperature do not differ significantly from one another. In favourable cases this makes it possible to assume as a first approximation that for two common-type reactions X and Y the standard entropy changes at a given temperature are equal, *i.e.* that

$$\Delta S_{X,T}^\circ = \Delta S_{Y,T}^\circ \qquad (15)$$

A second approximation, which makes allowance for the fact that the difference in the entropy change

$$\Delta S_{Y,T}^\circ = \Delta S_{X,T}^\circ = c \qquad (16)$$

is not equal to zero, but which assumes that it does not change with temperature (c = const) is more rigorous and has a wider use.

For reactions which are of the same type to a sufficient degree, this assumption usually shows good agreement with experimental data over a wide temperature range. At very high temperatures the agreement becomes less satisfactory when temperatures corresponding to the population of new vibrational levels or new levels of electronic excitation are approached. This assumption may not apply to reactions involving a change in the valence state of the elements being compared, since in the high-temperature range this may lead to a change in the nature of their chemical similarity. In many cases the results of the calculations can be improved by the double-comparison method. In the comparison of reactions of the same type, as in the comparison of substances of the same type, this method takes account of the fact that the difference c may change with temperature, but assumes that in two analogous pairs of reactions of the same type AX, AY and BX, BY the corresponding differences

$$\left.\begin{aligned} \Delta S_{AX,T}^\circ - \Delta S_{BX,T}^\circ = c_X \\ \Delta S_{AY,T}^\circ - \Delta S_{BY,T}^\circ = c_Y \end{aligned}\right\} \qquad (17)$$

change with temperature in the same way, *i.e.* that the difference ($c_X - c_Y$) can be taken as constant within a certain temperature range. Referring this constant to the values of S° at the temperature T_1, we obtain

$$(\Delta S_T^\circ - \Delta S_{T_1}^\circ)_{AX} - (\Delta S_T^\circ - \Delta S_{T_1}^\circ)_{BX} = (\Delta S_T^\circ - \Delta S_{T_1}^\circ)_{AY} - (\Delta S_T - \Delta S_{T_1}^\circ)_{BY}. \qquad (18)$$

This method requires a large number of data for the calculation, but it extends the applicability considerably and leads to a corresponding increase in the accuracy of the results; it can be regarded as a third approximation. It is possible in a similar fashion to compare the high-temperature components of the entropy change ($S_T^\circ - S_{298}^\circ$).

Relationships based on the assumption that the ratio of the entropy changes in two reactions of the same type are constant

$$\frac{(\Delta S_T^\circ - \Delta S_{T_1}^\circ)_Y}{(\Delta S_T^\circ - \Delta S_{T_1}^\circ)_X} = \alpha \quad \text{or} \quad \frac{\Delta S_{Y,T}^\circ}{\Delta S_{X,T}^\circ} = \alpha, \qquad (19)$$

analogous to those above and, more particularly, relationships analogous to Eqns. (7) or (9), in particular

$$\frac{(\Delta S_T^\circ - \Delta S_{T_1}^\circ)_{AX}}{(\Delta S_T^\circ - \Delta S_{T_1}^\circ)_{BX}} = \frac{(\Delta S_T^\circ - \Delta S_{T_1}^\circ)_{AY}}{(\Delta S_T^\circ - \Delta S_{T_1}^\circ)_{AY}}, \qquad (20)$$

also give on the whole quite satisfactory results. Their applicability is somewhat more restricted, however, and the accuracy of the calculation is usually lower than of that based on the assumption that c or the differences $c_X - c_Y$ are constant.

Similar equations can be derived for the enthalpy change for the reaction (the heat of reaction) ΔH.

Table 7 gives ΔS_T° (and the corresponding values of c and α) for the hydrolysis of CCl_4 and $SiCl_4$ in a reaction of the type $CCl_4 + 2H_2O = CO_2 + 4HCl$ and the corresponding reaction for $SiCl_4$, calculated from published data[28]. For the sake of comparison, the calculation for the hydrolysis reaction was carried out, nominally, for the gaseous state of SiO_2. (Recalculation for the crystalline and liquid states of SiO_2 for the corresponding temperatures can readily be

TABLE 7. Standard entropy changes ΔS°_T (cal deg^{-1} mole^{-1}) for the hydrolysis of carbon and silicon tetrachlorides as homogeneous gas reactions.

T, °K	Hydrolysis		c	a
	CCl_4	$SiCl_4$		
298.15	65.32	63.72	1.60	1.025
1000	63.98	63.24	0.74	1.012
2000	62.88	62.47	0.41	1.007
3000	61.64	61.24	0.40	1.007
4000	61.32	60.87	0.45	1.007
5000	60.70	60.17	0.53	1.009
6000	60.17	59.53	0.64	1.011

carried out from available data[28].) Here the possible error in the calculation of ΔS° from Eqn. (14) does not exceed 1 e.u. and is slightly higher in the calculation using α. The results cannot be improved by the double-comparison method using data for CF_4 and SiF_4. The calculation for the hydrolysis of CF_4 and SiF_4 itself gives approximately the same result, but the combination of these two pairs of reactions does not lead to any improvement, since the substances differ in four of the five atoms making up the molecule.

A similar picture is observed when comparing the values of $\Delta H^\circ_T - \Delta H^\circ_0$ and ΔH°_T and also the quantity a for the same reactions. For these reactions the method involving comparison of the ratios of the heats of reaction α cannot be used, since they have opposite signs and hence their absolute values change in opposite directions. The maximum error in the values calculated for 6000°K using a is here slightly greater than 1 kcal mole^{-1}.

No allowance was made here for the change in the heat of formation of SiO_2 (quartz) from ΔH°_{298} = 210 kcal mole^{-1}, given in standard tables[28] on the basis of published data[56], to the most recent value 217.7 kcal mole^{-1},[57,58] since this is not reflected in the results of the comparison.

For a very important class of reactions — formation from the elements (simple substances or free atoms) — however, the applicability of the above relationships at high temperatures is often very limited, since these reactions are always associated with a change in the valence state of the elements. For different valence states the analogy between the properties of given elements may not hold; in particular, the energies of the excited states and their temperature ranges are not the same. For many compounds of the same type the entropy of atomisation even at 6000°K shows simple relationships analogous to those described earlier[59-62] for less high and for ordinary temperatures.

A different kind of relationship is observed in the comparison of reactions of the same type not at the same temperature but at temperatures corresponding to equal values of the equilibrium constant K_a. With this method of comparison of any two chemical reactions X and Y (or phase changes), the difference in their standard entropy changes $\Delta S^\circ_X - \Delta S^\circ_Y$ is equal[63] to the difference in their entropy changes under equilibrium conditions $\Delta S_{X(equil)} - \Delta S_{Y(equil)}$ so that

$$\Delta S^\circ_X - \Delta S^\circ_Y = \frac{\Delta H^\circ_X}{T_X} - \frac{\Delta H^\circ_Y}{T_Y}. \qquad (21)$$

For reactions of the same type these differences are very small and affected little by temperature. Since the values of $\Delta H^\circ_X/T_X$ and $\Delta H^\circ_Y/T_Y$ are similar, their ratio $A = \Delta H^\circ_X T_Y / T_X \Delta H^\circ_Y$ also changes little with temperature. Thus for the dissociation of the diatomic molecules of the alkali metals at values of $\log K_a$ from -5 to +2 (corresponding to a temperature range of about 1000 deg for these reactions), the value of A for each pair of reactions changes by not more than 10%. At the same time the value of A in all these cases is close to unity. Hence one may assume that in comparing reactions of the same type, under conditions corresponding to identical values of the equilibrium constants, the parameters $\Delta H^\circ/T$ are numerically identical†.

$$\frac{\Delta H^\circ_X}{T_X} = \frac{\Delta H^\circ_Y}{T_Y} \qquad (22)$$

Table 8 gives, for several groups of reactions of the same type involving the dissociation of diatomic molecules to free atoms (and for certain reactions of this kind which are not of the same type), the values of $\Delta H^\circ/T$ for conditions corresponding to two values of the equilibrium constants ($\log K_{a,1}$ = -0.4771, corresponding to a degree of dissociation x_1 = 0.5, and $\log K_{a,2}$ = -5.0000, corresponding to x_2 = 0.00316), calculated from published data[28]. In each of these groups the values of $\Delta H^\circ/T$ in most cases are fairly close to one another but tend to increase slightly for reactions in which the given value of $\log K_a$ corresponds to a higher temperature. This manifests itself most markedly in the case of the hydrogen halides (here the degree to which the reactions are of the same type is also lower).

The ratio of the parameters $\Delta H^\circ/T$ corresponding to two values of the equilibrium constants naturally shows

TABLE 8. Ratio of the parameters of the dissociation of certain diatomic molecules to atoms under conditions corresponding to equal values of the dissociation constants ($\log K_{a,1}$ = -0.4771 and $\log K_{a,2}$ = -5.0000).

Substance	$\log K_{a,1} = -0.4771$		$\log K_{a,2} = -5.0000$		$\frac{T_1}{T_2}$	$\frac{\Delta H^\circ_2 T_1}{T_2 \Delta H^\circ_1}$	$\frac{\Delta H^\circ_2}{T_2} - \frac{\Delta H^\circ_1}{T_1}$
	T_1	$\frac{\Delta H^\circ_1}{T_1}$	T_2	$\frac{\Delta H^\circ_2}{T_2}$			
LiF	4881	29.53	2854	49.50	1.71	1.68	20.0
NaF	4199	28.57	2423	48.56	1.73	1.70	20.0
KF	4425	28.45	2535	47.86	1.75	1.68	19.4
LiCl	4246	27.87	2425	47.90	1.75	1.72	20.0
NaCl	3850	26.45	2155	46.73	1.79	1.77	20.3
KCl	4093	25.68	2260	45.94	1.81	1.79	20.3
CO	7147	37.50	4590	57.48	1.56	1.53	20.0
SiO	5681	35.46	3596	55.15	1.58	1.55	19.7
PbO	3428	29.64	1994	48.72	1.72	1.64	19.1
ZrO	5657	35.47	3532	54.03	1.60	1.52	18.6
BO	5648	33.91	3501	54.22	1.61	1.60	20.3
NO	4900	32.19	2972	52.33	1.65	1.63	20.1
SO	4019	31.98	2438	52.40	1.65	1.64	20.4
HF	4390	32.51	2676	52.65	1.64	1.62	20.1
HCl	3585	30.46	2129	50.53	1.68	1.66	20.1
HBr	3173	29.38	1853	49.56	1.71	1.69	20.2
HI	2687	28.09	1541	48.04	1.74	1.71	20.0
LiH	2356	25.21	1290	45.44	1.83	1.80	20.2

† This assumption is essentially analogous to Trouton's rule, but can be extended to any thermodynamic processes (phase transitions, chemical reactions, etc.) and to any case of identical values of the equilibrium constants, not merely those equal to unity. At the same time its use is restricted to reactions or processes of the same type, although it applies approximately to reactions and processes which are not strictly of the same type. Trouton's rule itself is also obeyed most closely in the comparison of substances of the same type and can also be extended[64-68] to pressures other than 1 atm. As for the dependence of Trouton's coefficient on boiling point, the same behaviour appears to apply to chemical reactions (see Table 8).

smaller variations. Since the values of ΔH° change more or less in parallel (and not very much in any case) with change in temperature, the above relationship leads to an approximate proportionality between the actual temperatures corresponding to the two values of the equilibrium constants. In Table 8 this corresponds to the result that the ratio T_1/T_2 is approximately constant for reactions which are to a sufficient degree of the same type. Constancy in the difference between the parameters $\Delta H^\circ/T$ corresponding to two values of the equilibrium constants is less affected by the degree to which the reactions are of the same type (see Table 8). Thus these relationships, previously established for ordinary and moderately high temperatures[63,69], are also applicable to high temperatures. Appreciable differences in excitation levels (for example for ZrO and PbO) may, however, lead to significant errors.

Many of the relationships and methods of calculation described by Karapet'yants[70,71] can undoubtedly be extended to the high-temperature range, probably with the same restrictions regarding the transition of atoms and molecules to excited states (for elements whose excitation levels differ appreciably) as those described above for the method of reactions of the same type.

IV. GASES AT VARYING PRESSURE

The degree of dissociation of gaseous substances decreases with increasing pressure if the dissociation process is accompanied by an increase in the number of molecules of gaseous substances.

For the dissociation of a molecule into two species (atoms, atomic groups, or ions), the dependence of the degree of dissociation x on the total pressure P for the case where the species formed are different, *i.e.* for reactions of the type AB = A + B, is given by the equation

$$x^2 = \frac{K_a}{K_a + P}, \qquad (23)$$

where K_a is the equilibrium constant; where the species are identical, *i.e.* for reactions of the type A_2 = A + A, the corresponding equation is

$$x^2 = \frac{K_a}{K_a + 4P}. \qquad (24)$$

The influence of pressure on the degree of atomisation of hydrogen at different temperatures is shown in Fig. 7.

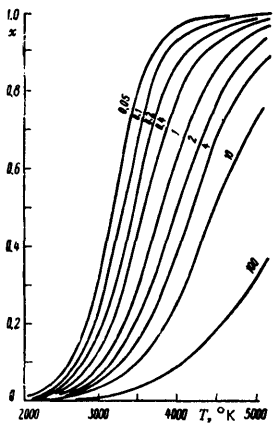

Fig. 7. Influence of pressure and temperature on the degree of dissociation x of hydrogen according to the reaction $H_2 = 2H$ at pressures of 0.05–100 atm.

V. PROCESSES OF VAPORISATION

Processes of vaporisation at high temperature have attracted considerable attention. This has been encouraged by the development of experimental methods for their study. Combining the technique of volatilisation from a surface or a Knudsen effusion chamber with mass spectrometry has made it possible to determine the masses of the species present in an equilibrium vapour and their relative concentrations. From the results of such determinations at several temperatures, it is possible to calculate the thermodynamic parameters for the vaporisation process. These methods have shown that vapours at high temperature often contain, in addition to simple species, various more complex species (see Table 9) whose number and concentration have been shown for many cases to increase with increasing temperature. Such data have been summarised[72].

These results have led to the view that at high temperatures the composition of vapours is complex and that the complexity of the species can increase with increase in temperature[1-3,10,23]. At the same time theoretical examination and factual material do not make it possible to assume that these conclusions are applicable to all systems (see below). The question as a whole has not yet been sufficiently studied. Increase in temperature always facilitates the dissociation of species to some extent, but for a saturated vapour increase in temperature is also associated with an increase in pressure, which suppresses the dissociation processes to a corresponding extent, which influence predominates in a given case and a given temperature range depends on the ratio of the heats of volatilisation and dissociation and on certain other parameters.

Processes involving an increase in the complexity of species (dimerisation, trimerisation, and polymerisation) at high temperatures may take place in the same temperature range as dissociation, and for processes which increase the complexity of the species, different directions and different degrees of displacement of the equilibrium composition of the saturated vapour with increase in temperature are possible, depending on the ratio of the corresponding parameters. Fig. 8 shows the influence of both

TABLE 9. Complex species in high-temperature vapours.

Condensed phase	Species in the gaseous phase*
LiF	LiF, $(LiF)_2$, $(LiF)_3$, $(LiF)_4$
LiOH	LiOH, $(LiOH)_2$, $(LiOH)_3$
NaOH+HCl	NaOH, $(NaOH)_2$, NaCl, $(NaCl)_2$, $Na_2(OH)Cl$
SiC	Si_2, Si_3, SiC_2, Si_2C, Si_3C, SiC, Si_2C_2, Si_3C_2
V_2O_5	V_4O_{10}, V_4O_8, V_6O_{14}, V_6O_{12}, V_2O_4
WO_3	$(WO_3)_3$, $(WO_3)_4$, $(WO_3)_5$
C	C, C_1, C_2, C_6, C_4, and a small number of more complex species
Ge	Ge, Ge_2 . . . Ge_6
$LiAlF_4$	$LiAlF_4$, LiF, $(LiF)_2$, AlF_3

* Detected for the most part as positive ions in the mass-spectrometer.

factors on the degree of dissociation of dimeric Na_2 molecules. The detailed mechanism for the formation of the equilibrium vapour and the nature of the dynamic equilibrium between it and the crystal (or melt) have not yet been studied.

The most important factor responsible for the presence of complex species in the vapour is the fact that, at high temperatures, atoms or groups of atoms (radicals) with unsaturated valences may take part in vaporisation. Complex species may then be produced as a result of the formation of covalent bonds between the species. In other cases the cause may be dipole–dipole interaction, for example in $(LiF)_2$. In addition, the transition of species to an excited state leads to the possibility of forming bonds which do not occur at ordinary temperatures, for example in the Mg_2 molecule, formed at high temperatures.

In each temperature range, vaporisation takes place by the rupture of those bonds which can be overcome by the thermal motion of the species at these temperatures. At low and ordinary temperatures volatilisation of liquids and crystals with molecular structures takes place. Substances consisting of complex molecules often cannot be heated without decomposition below their boiling points at normal pressure, since even at lower temperatures the thermal motion becomes capable of causing partial rupture of the bonds between the atoms in the molecules. At high temperatures almost the only materials which can remain in the condensed state are metals and substances with an ionic structure or with covalent bonds between the species, since these substances vaporise only under stronger thermal excitation.

The formation of complex species in the vapour is often observed in the volatilisation of individual metals (Li_2, Na_2, Cu_2, Ag_2, Mg_2, Ba_2, Pb_2, Sn_2–Sn_5, etc.). In ionic crystals and their melts and in crystals with covalent bonds, vaporisation may be associated with an increase in the complexity of the species or with chemical dissociation (in the case of compounds). Different groups of compounds show characteristic behaviour in this respect. Thus in the vapour of crystals consisting of singly-charged ions (alkali metal halides), thermal dissociation of the molecules takes place only at very high temperatures, whereas at lower temperatures the species increase in complexity as a result of dipole–dipole interaction. The increased complexity is restricted for the most part to the formation of dimers of the type $(LiF)_2$, and more complex species are formed only to a comparatively small extent[73–75]. Less frequently (CuCl) the preferential formation of trimers‡ of the type $(CuCl)_3$ and $(AgCl)_3$ is observed[76–78].

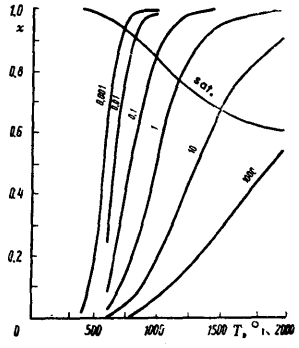

Fig.8. Influence of pressure and temperature on the degree of dissociation x of diatomic Na_2 molecules to atoms at pressures of 0.001–100 atm and the degree of dissociation of Na_2 molecules in the saturated vapour at different temperatures.

In lithium fluoride vapour at 900–1600°K the relative concentration of the dimer decreases[28] with increase in temperature (from calculated data) from 60–40 mole % above crystalline LiF to 20 mole % above the melt close to its boiling point, the concentration of the trimer decreasing at the same time. The decrease in the relative concentration of the dimer in LiCl vapour with increase in temperature follows approximately the same course[28]. With increase in temperature the concentration of the dimer in sodium chloride vapour increases above crystalline NaCl and decreases above the liquid. The particular nature of these relationships depends on the relationships between the values of the heats of sublimation, evaporation, and dimerisation, and other process of parameters.

The halides of metals of the lithium subgroup have heats of sublimation ΔH°_{298} equal to 47–66 kcal mole^{-1}, heats of dimerisation of the molecules ΔH°_{1000} equal to 32–62 kcal × × mole^{-1} and heats of dissociation of the diatomic molecules into atoms equal to 82–140 kcal mole^{-1}. With the exception of LiI, their boiling points lie above 1500°K.

Crystals consisting (formally) of doubly-charged cations and anions are naturally less volatile, because of the stronger interionic attraction. Out of the oxides of metals in the beryllium subgroup, only barium oxide vaporises to form BaO molecules (at 1530–1758°K) with almost no decomposition, plus a small quantity of Ba_2O, Ba_2O_2, and Ba_2O_3. Moderate decomposition accompanies the volatilisation of calcium oxide (65% at 1600–1750°K). The oxides of beryllium, magnesium, and strontium, however, are almost completely decomposed into atoms at about 2000°K. At the same time species such as $(BeO)_3$, $(BeO)_4$, $(BeO)_5$, $(BeO)_2$, and $(BeO)_6$ (in order of decreasing concentration) have been observed in small quantities in beryllium oxide vapour, the relative concentration of the more complex species increasing with increase in temperature. The heats of sublimation of these oxides ΔH°_0 decrease from 171.9 kcal mole^{-1} for BeO to 102 kcal mole^{-1} for BaO.[28] The heats of dissociation of the molecules into atoms ΔH°_0 increase from 100 kcal mole^{-1} for MgO to 137 kcal mole^{-1} for BaO.

Among the sesquioxides of the elements in the third group of the Periodic System, the rare-earth metals, and other metals, only boric oxide forms a vapour consisting chiefly of molecules B_2O_3. In the other cases[79–81] vapour formation is accompanied by chemical decomposition according to reactions of the type

$$M_2O_3(solid) \rightarrow 2MO(gas) + \frac{1}{2}O_2(gas), \quad (a)$$

or

$$M_2O_3(solid) \rightarrow M_2O(gas) + O_2(gas), \quad (b)$$

or

$$M_2O_3(solid) \rightarrow 2M(gas) + \frac{3}{2}O_2(gas). \quad (c)$$

‡ The earlier generally-held idea that copper monohalides are dimeric was based on the determination of their vapour densities, which characterise merely the average mass of the vapour species. Mass-spectrometric measurements showed, however, that in reality the vapour of copper(I) chloride consists chiefly of CuCl and $(CuCl)_3$ species, with a small concentration of $(CuCl)_2$.

Thus at about 2000°K, vaporisation takes place chiefly according to reactions of type (a) for Li_2O_3, Nd_2O_3, and Pr_2O_3; type (c) for Eu_2O_3; types (a) and (b) for Ti_2O_3 and Al_2O_3; and types (a) and (c) for Sm_2O_3.

A number of studies have been made of carbon in the vapour state[2,28]. It has been shown[82,83] on the basis of mass-spectrometric measurements that in the range 2000–2700°K the saturated vapour above graphite consists chiefly of species C_3, C_2, C_1, C_5, and C_4. Extrapolation of the experimental data leads to the conclusion that the ratios of the concentrations of these species in the saturated vapour at about 4000°K $C_3 : C_2 : C_1 : C_5 : C_4$ equals 4.5 : 2.8 : 1 : 0.5 : 0.35. A slight preponderance of species with an odd number of carbon atoms had already been established in several earlier studies. Pitzer and Clementi[84] carried out an approximate calculation of the basic thermodynamic functions up to 4000°K for these and more complex species on the assumption that they are made up of carbon atoms which are arranged linearly and joined by double bonds, using as a model carbon suboxide O=C=C=C=O. Although some of the conclusions reached in their work (in particular the result that the relative concentration of monatomic species increases at high temperatures) require confirmation, the work has revealed essentially the overall picture. It is undoubtedly true that a similar use of the molecules of di-, tri-, and poly-acetylenes and the corresponding cumulenes[85,86] as models, after experimental determination of their structural parameters and spectral data, will make it possible to obtain more complete information on the state of carbon species in the vapour. Mass-spectrometric measurements also give similar results for the nearest analogues of carbon, for which the vapours have been shown to contain polymeric species $Si_1 \ldots Si_7$, $Ge_2 \ldots Ge_8$, $Sn_2 \ldots Sn_5$, and Pb_2. The process of formation of complex species not from identical but from different monomeric species is of considerable interest. The formation of $Na_2(OH)Cl$ species in the volatilisation of NaOH and NaCl and of $LiAlF_4$ species in the volatilisation of LiF and AlF_3 have been described earlier[3,10,74]. The use of mass-spectrometry for the systematic study of the thermodynamic parameters of various processes occurring in related complex systems is, however, only just beginning. Thus Akishin and Sidorov[87–89] have determined various thermodynamic parameters for vaporisation in the $NaF–ZrF_4$ system, where, in addition to the simple species NaF and ZrF_4, the vapour also contains Na_2F_2 and $NaZrF_5$ species. The enthalpy of their dissociation into the component species NaF and ZrF_4 had the values 54.9 ± 2.2 kcal mole^{-1} for Na_2F_2 and 62.2 ± ± 4.6 kcal mole^{-1} for $NaZrF_5$. The use of mass-spectrometry should undoubtedly be extremely fruitful in studying the vapour composition of individual substances and also of more complex systems and solutions, not only at high temperatures but also at moderate and ordinary temperatures, particularly in examining association and chemical interaction in vapours.

Here we have given results from only a few of the papers devoted to the study of high-temperature vapours[2]. We have not dealt with the study of the structure of species in the vapour phase[2,28] or, in particular, with the work of Akishin and coworkers[90,91], which occupies a leading position in this field. Of the thermodynamic relationships for vaporisation, we have not considered the conclusions[1,2] reached by assuming that the entropy change is constant both for the volatilisation of different species and for corresponding dissociation processes of dimeric and more complex species. These assumptions make it possible to express approximately, in simple form, the relationship between temperature, the heat of the process, and the equilibrium pressure in processes of dimerisation, polymerisation, sublimation, and volatilisation. However, the limits of applicability of these relationships have not yet been adequately defined.

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HALIDES OF RARE-EARTH ELEMENTS IN A LOWER STATE OF OXIDATION

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I. INTRODUCTION

Until recently it was the commonly held opinion that in their compounds most of the rare-earth elements (r.e.e.) are exclusively tervalent, and that only some of them exhibit the so-called "anomalous" valencies of 2 and 4. This view was based mainly on studies carried out in the 1930's, when pure r.e.e. were available only with extreme difficulty, and experimental technique was at an insufficiently high level. However, their properties were so similar in all respects that the particular "anomalous" properties of some of them led to serious doubts, and investigators have never ceased the search for "anomalous" oxidation states in the other elements.

From this point of view, considerable interest attaches to the system of triply charged r.e.e. ions suggested by Klemm[1-3] on the basis of comparison of certain periodic properties of the r.e.e. (valency, colour of compounds, magnetic susceptibility) and constructed by analogy with the Periodic System of the elements:

$$\overset{\qquad\qquad\qquad\qquad\qquad\qquad La^{3+}}{Ce^{3+}Pr^{3+}Nd^{3+}Pm^{3+}Sm^{3+}Eu^{3+}Gd^{3+}},$$

$$Tb^{3+}Dy^{3+}Ho^{3+}Er^{3+}Tm^{3+}Yb^{3+}Lu^{3+}.$$

Here the ions La^{3+}, Gd^{3+}, and Lu^{3+} are analogous to the atoms of the inert gases in Mendeleev's Periodic System, their electron configurations being the most stable (empty, half-full, and full f shell). All the other triply--charged r.e.e. ions tend to lose or take up electrons so as to approximate to the most stable configuration. This systematisation of the r.e.e. graphically and in general correctly represents the tendency of lower and higher oxidation states of the r.e.e. to appear, and, what is most important, it gives an insight into the exclusive tervalency of some of the elements and the "anomalous" bivalent and quadrivalent states of the r.e.e., their valency being presented as a periodic function of atomic number.

R.e.e. compounds of lower oxidation state were first obtained at the beginning of this century, but they were not systematically investigated until the middle 1920's, when a series of works by Klemm, Jantsch, and others appeared. These investigated the preparation and chemical and physical properties of samarium, europium, and ytterbium dihalides and the possible existence of such forms with the other r.e.e., and developed methods for the isolation and purification of Sm, Eu, and Yb using compounds of these elements in, bivalent state. Although these papers give hardly any quantitative data on the processes and compounds studied, they contain considerable and interesting factual material on the chemistry of the r.e.e. dihalides.

Interest in this region of their chemistry has considerably increased in recent years because of the increased production of the rare-earth metals, which are normally obtained by electrolysis of the fused chlorides or metallothermic reduction of the anhydrous fluorides or chlorides. The reduction of the triply-charged ions in the melt must inescapably pass through intermediate stages, *i. e.* through ions of lower oxidation states. Knowledge of the properties of the resulting lower halides is necessary for the choice of optimum conditions for the process and to decrease losses in the electrolysis.

The use of differences in the stability of the compounds in the lower state of oxidation is also of promise for the separation of the r.e.e.

Several studies have now been published demonstrating the considerably widespread occurrence of the bivalent state among the r.e.e.

II. SHORT REVIEW OF THE CHEMISTRY OF COMPOUNDS OF RARE-EARTH ELEMENTS IN A LOWER STATE OF OXIDATION

1. Preparation and Some Properties of R. E. E. Dihalides

Of the r.e.e. dihalides, those of Sm, Eu, and Yb are the most stable. Until now the main method for their production has been the reduction of the anhydrous trihalides with hydrogen at elevated temperature[4]; this method is extremely lengthy and demands a number of precautions to prevent considerable contamination of the product with oxide halides and to ensure complete conversion of the trihalides to dihalides. In the production of diiodides by this method, the hydrogen is not so much the reducing agent (the heat of formation of HI is close to zero) as a carrier gas producing a more rapid dissociation of the triiodide.

In many cases it is more convenient to reduce the trihalides with various metals than with hydrogen.

Another method for obtaining the dihalides is the dissociation of the corresponding trihalides in a vacuum, and where applicable this is a more convenient method, since it does not require the production of very pure hydrogen.

The most universal method for the production of the dihalides is the reaction of the trihalides with the corresponding rare-earth metals[5-12], which provides all the known r.e.e. dihalides in the purest form.

In addition to the purity of the reactants, the production of the dihalides requires special care in the choice of material for the reaction vessel. When working with chlorides good results are obtained with metallic molybdenum or tantalum, which are sufficiently inert towards the fused rare-earth metals and their chlorides even at extremely high temperatures[13]; with iodides best results are obtained with metallic tungsten[11].

Brewer[14] has justifiably pointed out that some investigators did not take into account the interaction of the rare--earth metals and dihalides with the material of the vessel (gold, platinum, quartz). The rare-earth metals are known to form very stable intermetallic compounds with

gold and platinum; furthermore, when dissolved in the metal of the boat the activity of the rare-earth metal is greatly reduced. All this displaces the equilibrium towards disproportionation of the dihalide, the more so since the resulting comparatively volatile trihalide is removed from the reaction zone.

There is very scanty information on lower r.e.e. fluorides and bromides. Only the preparation and certain properties of the difluorides and dibromides of Sm, Eu, and Yb have been described[4]. Kirshenbaum and Cahill[15] investigated the reduction of yttrium, lanthanum, cerium, praseodymium, neodymium, and samarium trifluorides with graphite at 1300–2200°, and found that only SmF_3 is reduced, forming the red-brown SmF_2 of m.p. ~1400°. It was also shown that metallic tungsten or molybdenum does not reduce SmF_3 to SmF_2. There are no experimental thermodynamic data on r.e.e. difluorides or dibromides (as with the trifluorides or tribromides). One can only say, in accordance with known relative stabilities of lower and higher halides, that the difluorides should be less stable than the dichlorides, and that the dibromides should be intermediate in stability between the dichlorides and the diiodides.

As regards the latter, the preparation and some of the properties of r.e.e. diiodides, mainly those of Sm, Eu, and Yb, have been studied[4]. Thulium diiodide has only recently been obtained, by reduction of TmI_3 with metallic thulium[10]. This method has also been used to prepare YbI_2.[10] X-Ray crystallography has shown TuI_2 to have the YbI_2 structure.

Druding, Corbett, and their coworkers[9,11,12] have studied the equilibrium diagrams of the La–LaI_3, Ce–CeI_3, Pr–PrI_3, Nd–NdI_3, and Sm–SmI_3 systems, paying particular attention to the purity of the starting materials and absence of reaction with the material of the vessels. The triiodides were prepared from the metals and elemental iodine in a sealed evacuated quartz tube. The metal, in a tungsten crucible, was heated to 800° and the tube with the iodine to 185°. After the reaction the excess of iodine was removed by condensing it. All operations with the iodides and metals were carried out in a dry-box in an atmosphere of argon. Druding and Corbett emphasise[11] that the r.e.e. iodides are extremely sensitive to atmospheric oxygen and moisture. In the case of LaI_3 the product had to be sublimed in vacuum in tantalum apparatus to obtain satisfactory results.

Stable diiodides were obtained in all the systems. In the Nd–NdI_3 and Sm–SmI_3 systems the reduction goes beyond the composition corresponding to the diiodides, and products $NdI_{1.95}$ and $SmI_{1.91}$ were obtained. There was no indication of the existence of neodymium or samarium monoiodide. In the La–LaI_3 and Ce–CeI_3 systems there were observed, in addition to the diiodides, intermediate compounds, melting with decomposition, of the non-stoichiometric composition $LnI_{2.42}$; these were isomorphous with the compound $PrI_3 \cdot PrI_2$, which melts without decomposition, observed in the Pr–PrI_3 system.

The diiodides LaI_2, CeI_2, and PrI_2 are isomorphous, and differ in structure, melting points, colour, and other properties from the "normal" diiodides NdI_2, SmI_2, and YbI_2. While NdI_2 does not pass an electric current, LaI_2, CeI_2, and PrI_2 are good conductors, their electrical conductivity being ~10% of that of the pure metals. The magnetic moment of neodymium in NdI_2 corresponds to the doubly-charged ion Nd^{2+} (Pm^{3+}), while LaI_2 is only weakly paramagnetic.

All these unusual properties led Corbett *et al.*[11] to the conclusion that the diiodides LaI_2, CeI_2, and PrI_2 contain the normal triply-charged r.e.e. ions and free electrons forming a metallic bond, *i. e.* their structure is $Ln^{3+}e^-I_2^{2-}$, as in the previously observed r.e.e. sulphides and carbides. The additional energy of the metallic bond stabilises these diiodides against disproportionation into metal and triiodide.

It is a very interesting fact that, judging from the composition of the melt at the melting point of the diiodide, the stability of the diiodides decreases in the series LaI_2–PrI_2. Thus in the cerium group two tendencies in the stability of the diiodides are observed: the stability of the "normal" salt-like diiodides increases in the series La–Eu in accordance with the rapid increase in this series of the third ionisation potential (I_3) of the r.e.e. and the decrease in the energy of sublimation of the metal (see Table 2); the stability of the metal-like compounds increases in the reverse direction, since the decrease in I_3 in this direction favours the appearance of conductivity electrons in the salt lattice. The decrease in I_3 from europium to lanthanum correctly explains also the increased concentration of electron gas in lanthanum metal as compared with europium, *i. e.* the increase in the energy of sublimation from europium to lanthanum. Thus the heats of formation of these unusual metal-like compounds change within the r.e.e. group symbathically with the heats of sublimation of the metals, which is understandable, since these compounds and the metals both have substantially the same type of chemical bond (metallic).

Certain aspects of the chemistry of the r.e.e. dichlorides will be considered in more detail in Part III.

2. Oxide Chlorides, Oxides, and Chalcogenides of R. E. E. in a Lower State of Oxidation

Ivanovskii and coworkers[16] studied the reaction of oxygen and rare-earth metals with fused chlorides of La, Ce, Pr, and Nd, and in all cases observed the formation of red crystals of lower oxide chlorides, insoluble in water, and of composition close to Ln_2OCl_2.

The existence of the gaseous monoxides LnO was first established spectrographically, and then gaseous LaO was observed in mass-spectrometric investigations[17].

Achard[18-20] studied the action of graphite on the r.e.e. oxides. At 1600° and pressure below 10^{-3} mmHg, Sm, Eu, and Yb vaporise from a mixture of the r.e.e. oxides as the monoxides LnO, and this process can be used to isolate and separate these elements. Achard also showed[21,22] that EuO is formed in a mixture of Eu_2O_3 and graphite above 1300°. With excess of graphite the dark red EuO is produced, with a face-centred cubic lattice. The monoxide EuO melts above 1700° and distils in vacuum without decomposition. It is relatively stable in air and is only slowly decomposed by water. The oxide Eu_2O_3 vaporises rapidly at 2500° and 10^{-4} mmHg, the condensate being red-brown because of the presence of EuO.

Other r.e.e. monoxides have only been obtained under specific conditions of high vacuum and elevated temperatures. Goldstein, White, and their coworkers[23-25] have made a mass-spectrometric study of the vaporisation of La_2O_3 and Nd_2O_3 and the exchange of oxygen between La, Ce, Pr, and Nd and their monoxides; they found that La_2O_3 and Nd_2O_3 vaporise stoichiometrically at the com-

position $Ln_2O_{2.96}$. They detected the ions LnO^+, Ln^+, and O^+ in the vapour, the ions Ln^+ appearing at an energy of the ionising electrons greater than a certain definite value, *i. e.* their appearance is due to decomposition of the LnO molecules by electron bombardment. The composition of the vapour was different in the vaporatisation of Lu_2O_3 and Dy_2O_3; in the former case the vapour contained LuO and Lu, and in the latter case almost exclusively Dy; this is due to the lesser stability of the LuO molecules.

The values of ΔH° and ΔS° at ~2000°K were determined for the reactions:

$$Ln'(gas) + Ln''O(gas) \rightleftarrows Ln''(gas) + Ln'O(gas).$$

The calculation of the standard heats of formation from these data contains large errors because of the absence of thermal capacity data. For the gaseous monoxides of La, Ce, Pr, and Nd the values of ΔH° obtained were the same within the limits of experimental error, and were from -27 to -38 kcal. It is interesting that the energies of dissociation of the gaseous monoxides LaO, CeO, PrO, NdO, SmO, EuO, GdO, TbO, LuO, and YO [25] differ exactly by the difference in the heats of sublimation of the corresponding metals.

Shchukarev and Semenov[26] also investigated the composition of the vapour over the oxides of all the r.e.e. except Tm mass-spectrometrically, and showed that the volatility of their oxides in high vacuum and the composition of their vapour differ considerably for the oxides of different elements. There is a general tendency for the stability of the gaseous LnO molecules to decrease from La to Lu. In no case were ions $Ln_2O_3^+$ or $(LnO)_n^+$ observed in the vapour, but the ions CeO_2^+, PrO_2^+, and TbO_2^+ were detected over the corresponding oxides.

There are no data on the stability of the monoxides (except EuO) in the solid state at room temperature. Using the average value of the standard heat of formation of a gaseous monoxide LnO (-30 kcal mole^{-1} [23,24]) and assuming its heat of sublimation to be close to that of BaO and SrO (~120 kcal mole^{-1} [27]), we obtain a value of ~150 kcal mole^{-1} for the standard heat of formation of the solid monoxides of La, Ce, Pr, and Nd. To a first approximation, the monoxide can be considered to be stable in the solid state if ΔH° for the disproportionation into sesquioxide and metal is positive. If the heat of formation of Ln_2O_3 is taken as 430 kcal mole^{-1},[4] ΔH°_{298} for the reaction

$$3LnO \rightleftarrows Ln_2O_3 + Ln$$

is found to be 20 kcal mole^{-1}. Thus it may well be that some r.e.e. monoxides are also stable in the solid state at room temperature.

Klemm and Senff[28] prepared EuS, EuSe, and EuTe by heating $EuCl_2$ in a current of hydrogen with excess of S, Se, or Te, which was then removed by heating in a current of hydrogen at a higher temperature. Magnetic susceptibility measurements showed EuS, EuSe, and EuTe to be compounds with an ionic bond, containing the ions Eu^{2+}. Bivalent Sm and Yb also form monosulphides, and the sulphides Ln_3S_4 have been shown to contain the ions Ln^{2+} and Ln^{3+}.[29-31] The properties and structures of certain other compounds of the r.e.e. with non-metals of Groups V and VI have been described[32-34].

The monosulphides of the r.e.e. for which the bivalent state is less typical possess interesting electrical properties[35-40]; in particular, in the solid state they have considerable conductivity, close to that of the corresponding metals. Conductivity and magnetic susceptibility data on the solid monosulphides demonstrate that the lattice contains the normal triply-charged r.e.e. ions, and also electrons, which produce a metallic bond; these sulphides are therefore intermediate between ionic compounds and compounds with a metallic bond, and they have the general formula $Ln^{3+}e^-S^{2-}$. Certain r.e.e. acetylides in $Ln^{3+}e^-C_2^{2-}$ possess analogous properties[41-44]. As stated above, the diiodides of lanthanum, cerium, and praseodymium exhibit the same effect.

III. CHLORIDES OF RARE-EARTH ELEMENTS IN A LOWER STATE OF OXIDATION

The chemistry of the lower r.e.e. chlorides has been relatively fully investigated, but the existing quantitative data are very often approximate only.

1. Calorimetry of R. E. E. Dichlorides

Although the dichlorides of Sm, Eu, and Yb have been known for a comparatively long time, only one attempt has been made to determine their heats of formation calorimetrically[45-47]. The heats of solution of these dichlorides in 6 M HCl were determined in a microcalorimeter. It was found that $EuCl_2$ reacts very slowly with the HCl solution in the absence of air, while in the presence of air differing amounts of the Eu^{2+} ions undergo the side reaction:

$$Eu^{2+} + {}^1/_4O_2 + H^+ \rightarrow Eu^{3+} + {}^1/_2H_2O,$$

so that the heat of formation of $EuCl_2$ could not be determined. Atmospheric oxygen does not oxidise Sm^{2+} to Sm^{3+}, since identical results were obtained whether the acid was saturated with hydrogen or with air. With $YbCl_2$ there is only slight oxidation.

The dichlorides were obtained by reduction of the anhydrous trichlorides for 6 h at 650° with hydrogen. With samarium the reduction product contained only 69.4% $SmCl_2$. Since the heats of solution of metallic Sm and Yb are not known, the reduction potentials of Sm^{3+} and Yb^{3+} on a mercury cathode[48,49] were used in calculating the heats of formation of the dichlorides. The standard enthalpy of formation was calculated to be -195.6 kcal mole^{-1} for $SmCl_2$ and -184.5 kcal mole^{-1} for $YbCl_2$.

The enthalpy of formation of neodymium dichloride has been determined by dissolving the metal and the dichloride in 0.2 *N* HCl.[5,50] The $NdCl_2$ was prepared by melting the stoichiometric quantities of the trichloride and metal in molybdenum crucibles in an atmosphere of argon. The enthalpy of formation of $NdCl_2$ obtained, -163.2 kcal mole^{-1}, is in good agreement with the value calculated from the equilibrium diagram and pressure data in the Nd–$NdCl_3$ system[5,7].

2. Dissociation of Samarium, Europium, and Ytterbium Trichlorides

The dissociation of the fused trichlorides of Sm, Eu, and Yb with evolution of chlorine:

$$LnCl_3(liq.) \rightleftarrows LnCl_2(liq.) + {}^1/_2Cl_2(gas),$$

has been employed in the determination of the thermodynamic characteristics of the di- and tri-chlorides[50,51]. The equilibrium chlorine pressure was determined over the temperature range 600–960° with a quartz membrane

zero-manometer[52]. From the equilibrium chlorine pressure, and knowing the weight of chloride taken and the volume of the membrane chamber, the concentrations of the di- and tri-chlorides in the melt were calculated, and hence the corresponding equilibrium constants, from which ΔF°, ΔH°, and ΔS° for the dissociation were obtained.

At the average temperature of ~800° ΔH° for the dissociation is 28.8 kcal for $SmCl_3$, 11.6 kcal for $EuCl_3$, and 24.0 kcal for $YbCl_3$, and ΔS° for all three chlorides is close to 9 entropy units. The calculation of the standard heats of formation of the dichlorides of Sm, Eu, and Yb included the use of the standard enthalpies of formation of $SmCl_3$ (-243 kcal mole^{-1}), $EuCl_3$ (-241 kcal mole^{-1}), and $YbCl_3$ (-223 kcal mole^{-1}) obtained by interpolation of the data for the trichlorides of the other r.e.e.,[53,54] and also the approximate value of ΔC_p for the dissociation, equal to -12 kcal mole^{-1} deg^{-1} in the temperature interval 25–900°. The standard enthalpies of formation obtained[50,51] were -203 kcal mole^{-1} for $SmCl_2$, -217 kcal mole^{-1} for $EuCl_2$, and -186 kcal mole^{-1} for $YbCl_2$. The value for $SmCl_2$ is closer to Brewer's estimate (-203 ± 7 kcal mole^{-1} [14]) than to the calorimetrically determined value of -195.6 kcal × × mole^{-1}. The value obtained for $EuCl_2$ is also close to Brewer's estimate (-210 ± 7 kcal mole^{-1} [14]), but the value obtained for $YbCl_2$ is in good agreement with the value of -184.5 kcal mole^{-1} determined calorimetrically. The dissociation of the trichlorides has also provided a value for the absolute entropy S°_{298} of the trichlorides (34 entropy units), taking S°_{298} for the dichlorides as 32 entropy units. The thermodynamic data obtained can be used in considering certain equilibria in which the di- and tri-chlorides of Sm, Eu, and Yb take part.

The anhydrous r.e.e. trichlorides are normally prepared by chlorination of the corresponding oxides[7,55]. With $SmCl_3$, $EuCl_3$, and $YbCl_3$ there is the danger of their partial dissociation to form the dichlorides as impurities. Calculation shows that in the case of chlorination in a current of chlorine ($P_{Cl_2} \simeq 1$ atm) the fused trichlorides near their melting points will contain the following amounts of dichloride (in mole %): $SmCl_3$ 0.005, $EuCl_3$ 8, and $YbCl_3$ 0.1. Under these conditions $SmCl_3$ and $YbCl_3$ will be obtained sufficiently pure, even if chlorination is carried out in the fused state, while $EuCl_3$, which because of its low melting point is usually obtained in the fused state, must be finely ground and heated in the current of chlorine but not so as to melt it. The solid $EuCl_2$ should then be fully converted into $EuCl_3$, since the chlorine pressure over the solid trichlorides of these elements is considerably lower (where no solid solutions are formed) than over the fused trichlorides, being at 620° 5×10^{-7} mmHg for $SmCl_3$, 5 mmHg for $EuCl_3$ and 2×10^{-5} mmHg for $YbCl_3$. In a vacuum solid $EuCl_3$ should completely dissociate into $EuCl_2$. In the fused state $SmCl_3$ and $YbCl_3$ also dissociate to the dichlorides to a considerable extent in a vacuum.

Reduction of the trichlorides with hydrogen is the usual method for the preparation of $SmCl_2$, $EuCl_2$, and $YbCl_2$. The free energy change ΔF° for the reduction of solid $SmCl_3$, $EuCl_3$, and $YbCl_3$ with hydrogen:

$$LnCl_3 + {}^1/_2H_2 \rightleftarrows LnCl_2 + HCl$$

at 620° is respectively -5, -20, and -9 kcal. Taking into account the formation of the intermediate compound $LnCl_3 . nLnCl_2$ in the $LnCl_2$–$LnCl_3$ systems[7,50], it is doubtful whether solid $SmCl_3$ can be completely reduced. Reduction in the melt should theoretically go to completion, but in the case of $SmCl_3$ the rate of the reaction is apparently too low. In most cases reduction of the trichlorides of the other r.e.e. can be ignored. Calculation using the approximate heats of formation of the dichlorides shows[5] that marked reduction can only be expected in the case of the chlorides of Nd, Pm, Er, Tm, and Sc.

3. Equilibrium Diagrams of Rare-Earth Metal–Trichloride Systems

The dichlorides of the other r.e.e. are less stable than those of Sm, Eu, and Yb, and can be obtained by reduction of the trichlorides with the corresponding rare-earth metal. Study of the equilibrium diagrams of Ln–$LnCl_3$ systems can not only demonstrate the existence of the dichlorides, but can also give certain information on the interaction between the tri- and di-chlorides in the solid state and in the melt, and when the dichloride melts incongruently its approximate heat of formation can be calculated. The study of these systems is complicated by the high reactivity of the dichlorides and the metals. The melt is usually held in molybdenum or tantalum apparatus in an atmosphere of carefully purified argon or helium; other metals or ceramics are unsuitable for use in these investigations. The attention which must be directed towards the experimental technique can be judged from the measurements of conductivity in the Ce–$CeCl_3$ system[56–58], where reaction of the melt with the material of the container completely distorted the results.

At present, equilibrium diagrams have been obtained for the systems La–$LaCl_3$,[59] Ce–$CeCl_3$,[60] Pr–$PrCl_3$,[7,50,61,86], Nd–$NdCl_3$,[7–9,50] Sm–$SmCl_3$, Y–YCl_3, and Sc–$ScCl_3$.[6,50]

There is no evidence of the formation of any chemical compound of lower oxidation state in the La–$LaCl_3$, Ce–$CeCl_3$, or Y–YCl_3 systems. The solubility of the metal at the eutectic point is respectively 9 (826°), 9.3 (777°), and 2 mole % (716°).

In the Pr–$PrCl_3$ system an unstable intermediate compound is formed, apparently of composition $PrCl_3 . PrCl_2$, and existing in the solid state in the narrow temperature interval 665–640°. Below 640° it decomposes into solid $PrCl_3$ and metal. X-Ray diffraction could detect no compounds of lower oxidation state in this system at room temperature[8]. There is a report[62] that an unstable intermediate compound has been observed in this system.

In the Nd–$NdCl_3$ system[8,9], $NdCl_2$ melting with decomposition has been observed, and also two intermediate compounds of composition $NdCl_{2.27}$ and $NdCl_{2.37}$. It has been shown by X-ray diffraction that $NdCl_2$ is isomorphous with $SmCl_2$ and $EuCl_2$. This system has also been investigated by Polyachenok[7,50], who confirmed the formation of the stable dichloride $NdCl_2$. The stoichiometric compositions $NdCl_3 . 2NdCl_2$ and $NdCl_3 . 3NdCl_2$ were found for the intermediate compounds.

The dichloride $SmCl_2$ melting at 859° is formed in the Sm–$SmCl_3$ system[6,50], and also the intermediate compound $SmCl_3 . 4SmCl_2$. The $SmCl_2$ obtained by fusing $SmCl_3$ with metallic Sm differs in appearance and melting point from the $SmCl_2$ obtained by hydrogen reduction of $SmCl_3$, and is very like $NdCl_2$.

Just as in the Nd–$NdCl_3$ system, a phase transformation has been observed in the Sm–$SmCl_3$ system in the region of compositions Sm–$SmCl_2$, lying below the melting point of the dichloride. No satisfactory explanation of this effect

has yet been given, but at any rate it demonstrates the complex nature of $NdCl_2$ and $SmCl_2$. These are apparently transitional between the normal dichlorides $EuCl_2$ and $YbCl_2$ and the metal-like compounds observed with the iodides[11]. The possibility of these transformations being associated with further reaction between the dichlorides and the metals is also not excluded. From this point of view the study of the Eu–$EuCl_2$ and Yb–$YbCl_2$ systems formed by the salt-like dichlorides of europium and ytterbium is of interest.

The dichloride $ScCl_2$, melting with decomposition, has been observed in the Sc–$ScCl_3$ system[6,50], and also an intermediate compound of composition $2ScCl_3.ScCl_2$. Barber and coworkers[63] had previously calculated the heat of formation of $ScCl_2$ by the Born–Haber cycle, and concluded that $ScCl_2$ should not be very stable. The heat of formation of $ScCl_2$ calculated from the equilibrium diagram data is 145 kcal $mole^{-1}$.[6,50,51]

4. Saturated Vapour Pressure in Rare-Earth Metal–Trichloride Systems

Another method of investigation of the lower r.e.e. chlorides is the measurement of the saturated vapour pressure over the fused trichlorides containing the dissolved metal. Information on the solubility of the rare-earth metals in the melt at elevated temperature is obtained at the same time. Novikov and Polyachenok[64,65] developed a variation of the "boiling point" method suitable for this purpose, and measured the pressure of the saturated vapour in the Sc–$ScCl_3$, Y–YCl_3, La–$LaCl_3$, Pr–$PrCl_3$, Nd–$NdCl_3$, and Er–$ErCl_3$ systems in the temperature range 1000–1400°.[6,7,50,51,66] The quartz ampoules employed were coated inside with a dense layer of metallic molybdenum by reduction of $MoCl_5$ vapour with hydrogen[67]. These ampoules enable a point to be obtained on the equilibrium diagram with a sample of only 0.2–0.5 g, with measurement of the saturated vapour pressure at any desired temperature up to 1400°.

The saturated vapour pressure *vs.* composition isotherms obtained with the systems named can be divided into three types.

In the La–$LaCl_3$ and Y–YCl_3 systems the experimental points, right up to the region of stratification, lie on a straight line intersecting the composition axis at the point corresponding to the metal. This corresponds to atomic dissolution of the metal, or dissolution by the Bredig mechanism[62]:

$$Ln(solid) \rightleftarrows Ln^{3+}(liq.) + 3e^-.$$

The Nd–$NdCl_3$ and Er–$ErCl_3$ systems exhibit only slight positive or negative deviations from the line intersecting the composition axis at the composition corresponding to the dichloride, *i. e.* the doubly-charged ions Nd^{2+} and Er^{2+} are formed in the melt.

The Pr–$PrCl_3$ and Sc–$ScCl_3$ systems are intermediate in type. On the basis of the information available, it is difficult to say whether this is due to the simultaneous presence of doubly-charged ions and free electrons (Bredig mechanism) in the melt or to dimerisation of the doubly-charged ions, and, apparently, Bredig's data[62] on the conductivity of the melts in the La–$LaCl_3$, Pr–$PrCl_3$, and Nd–$NdCl_3$ systems cannot distinguish between the two mechanisms.

In all cases only the corresponding trichlorides were observed visually in the distillate, the dichlorides $PrCl_2$, $NdCl_2$, $ErCl_2$, and $ScCl_2$ being unstable in the vapour at the temperatures indicated, and disproportionating exothermically into the corresponding gaseous trichloride and molten metal. The heats of vaporisation of the trichlorides from melts not saturated with respect to the metal are close to the heats of vaporisation of the pure trichlorides[50,68]. Assuming that with Sc, Pr, Nd, and Er all the metal is present in the melt as the dichloride, the equilibrium constant of the disproportionation reaction

$$3LnCl_3(liq.) \rightleftarrows 2LnCl_4(liq.) + Ln(liq.)$$

can be calculated and ΔS° for the reaction evaluated, and the heat of formation of the dichloride can be determined. Calculations using the average thermal capacities of the components have given values close to those obtained from the equilibrium diagrams.

In the Pr–$PrCl_3$ and Nd–$NdCl_3$ systems it was possible to construct saturated vapour pressure *vs.* melt composition isotherms for several temperatures, so that ΔF°, ΔH°, and ΔS° for the disproportionation at the mean experimental temperature of 1250° could be calculated. For the above disproportionation of the dichlorides, ΔH° is 24 ± ± 10 kcal for $PrCl_2$ and 38 ± 10 kcal for $NdCl_2$, with ΔS° = = 15 entropy units for both dichlorides.

The conversion to standard conditions of the thermodynamic data obtained at high temperatures introduces considerable errors, because of the almost complete absence of experimental data on the thermal capacities of the reaction components; however, the heat of formation of $NdCl_2$ determined calorimetrically is in good agreement with the value calculated by the method indicated above from equilibrium diagram and vapour pressure data[5,50].

5. Saturated Vapour Pressure of Samarium, Europium, and Ytterbium Dichlorides

We have measured[50,51] the saturated vapour pressure of the pure dichlorides $SmCl_2$, $EuCl_2$, and $YbCl_2$ over the temperature range 1200–1400°; $SmCl_2$ was obtained by fusing stoichiometric amounts of $SmCl_3$ and metallic Sm, and $EuCl_2$ and $YbCl_2$, by reducing the trichlorides with metallic zinc.

The r.e.e. dichlorides have very low volatility, the saturated vapour pressures at the maximal experimental temperature of 1400° being ~10 mmHg for $SmCl_2$, ~3 mmHg for $EuCl_2$, and ~5 mmHg for $YbCl_2$. Only with $SmCl_2$, therefore, could the heat of vaporisation be found with satisfactory accuracy (60 kcal $mole^{-1}$ at the mean temperature of 1300°), while with $EuCl_2$ and $YbCl_2$ the heats of vaporisation were calculated from the experimental results on the saturated vapour pressure by assuming ΔS for the vaporisation of these dichlorides to be the same (at the corresponding vapour pressure) as that for $SmCl_2$.

The boiling points of $SmCl_2$, $EuCl_2$, and $YbCl_2$ are 1950°, 2100°, and 2050°. The change in volatility in the series $SmCl_2$–$EuCl_2$–$YbCl_2$ does not follow the increase in atomic number of the metal, as is found with the r.e.e. trichlorides, but obeys the rule that the less stable the dichloride, the greater its volatility. This suggests that it is not the dichlorides themselves which vaporise, but their disproportionation products: the metals and trichlorides, which recombine to form the dichlorides in the

cooler parts of the apparatus (only the dichlorides are observed visually in the distillate). However, approximate thermodynamic calculations do not confirm this suggestion, particularly in the case of $EuCl_2$ and $YbCl_2$.

It may also be thought that this volatility relationship is a consequence of the nature of the dichlorides themselves, and in fact if the boiling points of the fluorides of elements of Group II of the Periodic System are compared[69] with the ionic radii of the corresponding doubly-charged cations, it is seen that the boiling points for the alkaline earth metal difluorides lie on a smooth line with a maximum at an ionic radius of 1.1–1.2 Å; the alkaline earth metal dichlorides also show a maximum boiling point at this ionic radius[69]. From this aspect the appearance of a maximum boiling point in the r.e.e. dichlorides around $EuCl_2$ (the ionic radius of Eu^{2+} is 1.24 Å) falls in with the general properties of the dihalides.

6. Electrical Conductivity and Density in Rare-Earth Metal–Trichloride Systems

Investigation of the electrical properties of melts containing dissolved metals is a common and convenient method for studying the nature of the melts and thermodynamic characteristics of lower halides if they are formed when the metals dissolve[70,71].

In their investigation of e.m.f., density, and conductivity in the Ce–$CeCl_3$ system, Mellors and Senderoff[56,72] concluded that the metal dissolves in the $CeCl_3$ to form Ce^+ ions, but this was later shown to be incorrect[57], because the melt was in contact with Al_2O_3. Bredig and coworkers[58,62] repeated the conductivity measurements in this system, and investigated the La–$LaCl_3$, Pr–$PrCl_3$, and Nd–$NdCl_3$ systems similarly. The conductivity of the melt, in the case of lanthanum and cerium, increases sharply when the metal is added, which can only be explained by the formation of free electrons in the melt, by ionisation of the atoms of dissolved metal:

$$\mathrm{Ln(solid)} \rightleftarrows \mathrm{Ln^{3+}} + 3e^- \text{ or } \mathrm{Ln(solid)} \rightleftarrows \mathrm{Ln^{2+}} + 2e^-.$$

In the Nd–$NdCl_3$ system the conductivity increases only very slightly as the concentration of metal is increased, *i. e.* there is practically no dissociation of Nd^{2+} ions into Nd^{3+} and e^-. The Pr–$PrCl_3$ system occupies an intermediate position, but is much closer to the Nd–$NdCl_3$ system. It has been suggested[62] that this demonstrates the existence of Pr^{2+} ions in the melt, of similar stability to the Nd^{2+} ions.

TABLE 1. Some characteristics of r.e.e. di- and tri-chlorides.

Element	$-\Delta H^\circ_{298}$ (kcal mole^{-1}) for the formation of dichloride	$-\Delta H^\circ_{298}$ (kcal mole^{-1}) for the formation of trichloride	Melting point of the dichlorides, °C
Sc	145 [50,51]	221 [76]	805(decomp.) [6,80]
Pr	163 [50,51]	252 [54]	—
Nd	163.2 [5,50]	246.5 [5,50]	835(decomp.) [7,80]
Sm	203 [50,51]; 195.6 [45]	243 *	859
Eu	217 [50,51]	241 *	738 [50]
Er	150 [50]	229 [54]	—
Yb	186 [50,51]; 184.5 [45]	223 *	723 [4]

* Extrapolation of Spedding's data[54].

Attempts have also been made[73–75] to provide a theoretical foundation for the effects observed on the dissolution of the metals in the fused halides.

Table 1 collects together the available standard enthalpies of formation of the solid r.e.e. dichlorides and the corresponding trichlorides; in most cases the values for the dichlorides have been calculated from those for the trichlorides. The melting points of the dichlorides given in Table 1 demonstrate that like the diiodides[11] they fall into two groups which have different physical and chemical properties: the comparatively unstable $ScCl_2$, $NdCl_2$, and $SmCl_2$, which have relatively high melting points and are black lustrous crystalline substances, and the more stable $EuCl_2$ and $YbCl_2$, which melt at a comparatively low temperature.

IV. POSSIBILITY OF EXISTENCE OF RARE-EARTH ELEMENT DIHALIDES

The experimental chemistry of lower r.e.e. halides which has been reviewed shows that work in this field is really only just beginning, and that there are no experimental data for the halides of many of the r.e.e., especially the fluorides and bromides. All the elements of the cerium group form diiodides. Judging by the ionisation potentials and energies of sublimation of the metals, the relationships observed in the cerium group should also apply to the elements of the yttrium group, so that diiodides would be expected to be formed by all the elements of the yttrium group and yttrium and scandium. Of these, ScI_2 and ErI_2, together with the known TmI_2 and YbI_2, will apparently be "normal" diiodides, while the others will possibly be metal-like compounds. The metal-like compounds of the yttrium group should be less stable than those of the cerium group, since I_3 for the yttrium group elements is somewhat higher.

With the r.e.e. dibromides also, typical salt-like and metal-like compounds should apparently be found.

Metal-like r.e.e. dichlorides have not been and can hardly be expected to be found in so clearly expressed a form as in the diiodides ($NdCl_2$, $SmCl_2$, and $ScCl_2$ retain only some indications of this type of compounds, *e.g.*, colour), probably because the chlorine atom has a greater affinity for the electron than the iodine atom. In actual fact, in the fused state the differences largely disappear[11], and solutions of La and Ce in the fused trichlorides are true ionic-electronic liquids[77].

It is improbable that metal-like compounds will be found among r. e.e. fluorides.

Since for r.e.e. dichlorides and difluorides the component of the energy of formation associated with the presence of the additional metallic bond in the crystal can apparently be ignored, the heats of formation of the salt-like (ionic) dihalides can be calculated[5] from the Born–Haber cycle, using Kapustinskii's equation for calculating the energy of the crystal lattice†:

$$Q = U + 2E - \sigma - D - \Sigma I_1 + I_3,$$

where U is the crystal lattice energy, E is the electron

† The errors arising in such an approximate calculation, which may be particularly large in the case of the fluorides, are to a large extent systematic in nature when the variation in stability throughout the rare-earth group is being considered.

affinity of the halogen atom, σ is the heat of sublimation of the metal, D is the dissociation energy of the halogen molecule, and $\Sigma I_1 + I_2$ is the sum of the first and second ionisation potentials of the r.e.e. atoms.

As early as 1950 Brewer[14] tried to assess the possibility of obtaining certain r.e.e. dichlorides, and suggested that in addition to $SmCl_2$, $EuCl_2$, and $YbCl_2$, the stable $NdCl_2$ and $TmCl_2$ and the unstable $PrCl_2$. $HoCl_2$, and $ErCl_2$ would be obtained. He also suggested that the r.e.e. monohalides are unstable. Our calculations have confirmed that all the r.e.e. monohalides must disproportionate strongly exothermically into the trihalide and the metal[5].

The best agreement of the calculated crystal lattice energies with existing experimental data was obtained for the trichlorides with the normal, and in the case of the dichlorides, with the improved Kapustinskii equation[78]. In calculations with the fluorides the improved Kapustinskii equation was also only used for the difluorides.

Since the radii of the doubly-charged r.e.e. ions are only known for samarium, europium, and ytterbium, in calculating the crystal lattice energy we have used the approximate radii obtained by analogy with the ion pairs $Sm^{2+}-Sm^{3+}$, $Eu^{2+}-Eu^{3+}$, and $Yb^{2+}-Yb^{3+}$.

The quantity $2E-D$ was taken as 118 kcal for the dichlorides and 130 kcal for the difluorides[79]. The heats of sublimation of the metals have been determined by Spedding and White and their coworkers[80-82].

Data obtained for the first ionisation potentials[83-85] indicate values of 5.6 ± 0.1 eV for cerium group elements and 6.2 ± 0.2 eV for yttrium group elements. The existing data on the second ionisation potentials of the cerium group elements[83] and those calculated by the Born–Haber cycle from thermodynamic data enable $\Sigma I_1 + I_2$ to be taken as constant for all the cerium group elements, and equal to 16.9 ± 0.3 eV. For the yttrium group elements $\Sigma I_1 + I_2$ was also taken to be constant at 18.9 eV.

Table 2 gives the approximate heats of formation of the dichlorides and difluorides that we have calculated by the above method, and also the corresponding heats of formation of the trichlorides found experimentally[53,54] or by interpolation of experimental data.

The heats of formation of the trifluorides were calculated from the thermochemical cycle, using the values of the sum of the three ionisation potentials of the r.e.e. $\Sigma I_1 + I_2 + I_3$ obtained, using the same cycle, from the heats of formation of the corresponding trichlorides.

The heats of formation of only the difluorides and dichlorides are as yet insufficient to assess their stability. For this it is necessary to consider the disproportionation of the dihalides into metal and the stable trihalide, *i.e.* the reaction:

$$3LnX_2(\text{solid}) \rightleftarrows 2LnX_3(\text{solid}) + Ln(\text{solid}).$$

The heats of disproportionation of the difluorides and dichlorides are also given in Table 2.

Certain qualitative conclusions can be drawn from Table 2 regarding the stability of the r.e.e. dichlorides and difluorides:

(1) In addition to the known $NdCl_2$, $SmCl_2$, $EuCl_2$, $YbCl_2$, and $ScCl_2$, the stable $PmCl_2$ and $TmCl_2$ may also be obtained.

(2) Of the less stable dichlorides, $HoCl_2$ and $ErCl_2$ may apparently be obtained in the solid state, in addition to the known $PrCl_2$.

(3) The dichlorides $LaCl_2$, $CeCl_2$, $GdCl_2$, $TbCl_2$, and YCl_2 are not expected to be formed in the solid state. These compounds, or more accurately the ions La^{2+}, Ce^{2+}, Gd^{2+}, Tb^{2+}, and Y^{2+}, apparently do not exist in the melt.

(4) Of the difluorides, apparently only SmF_2, EuF_2, and YbF_2 are stable at room temperature. There may be indications, however, that at high temperatures compounds intermediate between LnF_2 and LnF_3 may be produced in the case of scandium, thulium, and promethium. The formation of other r.e.e. difluorides must be considered improbable.

TABLE 2. Calculation of the stability of r.e.e. dihalides.

Element	σ, kcal per g-atom	Ionic radius, Å		Ionisation potentials			$-\Delta H^\circ_{298}$ (kcal mole^{-1}) for					
		r^{3+}	r^{2+}	$\Sigma I_1 + I_2$	$\Sigma I_1 + I_2 + I_3$	I_3	formation of dichloride	formation of trichloride	disproportionation of dichloride	formation of difluoride	formation of trifluoride	disproportionation of difluoride
La	97	1.22	1.38	390	832	443	128	256	128	213	435	231
Ce	96	1.18	1.36	390	848	459	131	253	113	217	435	219
Pr	78	1.16	1.31	390	873	482	156	252	36	244	436	140
Nd	76	1.15	1.29	390	884	494	161	246	9	250	431	112
Pm	62	1.14	1.27	390	901	510	178	246	— 42	268	432	60
Sm	50	1.13	1.26	390	919	528	192	243	—102	282	431	16
Eu	42	1.13	1.24	390	929	540	200	241	—118	294	429	—24
Gd	84	1.11	1.22	436	894	459	117	240	129	209	430	233
Tb	87	1.09	1.19	436	901	466	118	236	118	212	428	220
Dy	62	1.07	1.16	436	945	510	148	233	22	243	418	107
Ho	70	1.05	1.13	436	936	501	145	231	27	241	427	131
Er	66	1.04	1.12	436	945	510	150	229	8	247	426	111
Tm	58	1.04	1.11	436	956	519	159	226	— 25	257	423	75
Yb	40	1.00	1.06	436	990	554	185	223	—109	286	425	—8
Lu	95	0.99	1.04	436	940	503	133	221	43	235	425	145
Y	97	1.06	1.12	436	903	466	119	233	109	216	429	210
Sc	79	0.83	0.9—1.0	447	1012	565	151[63]	221	— 11	272	445	74

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PROCESS IN THE SYNTHESIS OF MACROCYCLIC AND OTHER PERFUMERY MATERIALS

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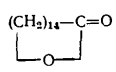
I. MACROCYCLIC PERFUMERY MATERIALS

Perfumery materials of macrocyclic structure are highly esteemed in the industry, and it is natural that the development of preparative methods for these compounds and the study of their properties should continue to attract the attention of chemists. In addition to papers describing new syntheses of macrocyclic compounds, an increasing number of papers and patents are being published which describe successful solutions of practical problems. It is with these reports, which greatly extend the opportunities for large-scale production, that we shall begin a review of recent achievements in the chemistry of macrocyclic perfumery materials.

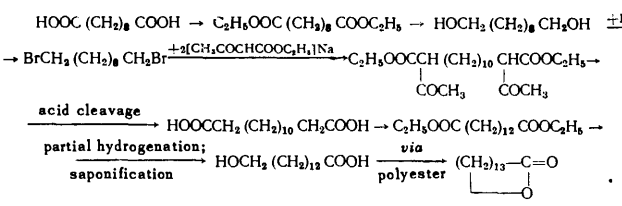
The compound which has acquired the greatest practical importance among macrocyclic compounds is pentadecanolactone,



It is marketed under the trade names Exaltolide and Thibetolide, among others, and has exceptional perfuming properties, imparting fragrance and persistence and tending to "ennoble" a whole composition. Moreover, the methods that have been developed for preparing macrocyclic lactones are very convenient compared with those used for other macrocyclic compounds.

Papers describing very simple and convenient methods for converting ω-hydroxy-acids into macrocyclic lactones have already been noted[1]. The main problem in the development of an industrial method of preparing pentadecanolactone and similar macrocyclic lactones has been reduced to a search for the most efficient route to the ω-hydroxy-acids required. In recent years several papers have been devoted to a solution of this problem. Several methods of synthesising hydroxyalkanoic acids have been developed at the All-Union Research Institute for Synthetic and Natural Perfumery Materials (VNIISNDV). In one of these the carbon skeleton of the hydroxy-acid is built up by condensing an αω-dihalogeno-derivative with two molecules of ethyl acetoacetate. Acid cleavage of the condensation products leads to an αω-dicarboxylic acid containing four carbon atoms more than the initial dihalogeno-derivative.

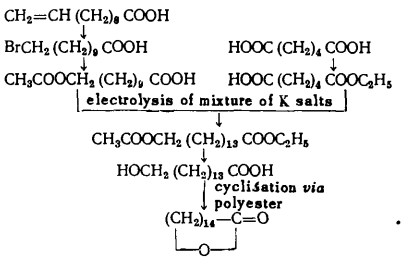
When a convenient method had been developed for the preparation of alkylacetoacetic esters by direct alkylation of sodium acetoacetic ester (prepared by ester condensation of ethyl acetate [and (?)] sodium [ethoxide (?)], which is obtained from alcohol and alkali[2]), this production stage presented no fundamental difficulties. This route was used for the preparation of tetradecanolactone, the next lower homologue of Thibetolide:



The tetradecanolactone obtained in this way has the persistent odour of musk and sandalwood[3].

In other methods for extending the carbon chain developed at VNIISNDV, salts of monoesters of dicarboxylic acids are electrolysed, when the acid radicals combine. Work in which two like acid residues were condensed electrolytically has been considered in a previous review[1]; this route was used for the preparation of hexadecanolactones, the next higher homologue of Thibetolide. Hexadecanolactone has a musk odour somewhat weaker but "softer" than that of Thibetolide[3].

Another electrochemical method of lengthening the carbon chain consists in the "cross" condensation of radicals of two different acids. This procedure is the basis of a method worked out at VNIISNDV[3-5] for the synthesis of pentadecanolactone; the general scheme may be represented



If electrochemical condensation is accomplished in one of the later stages of the synthesis (compared, for example, with the possible method of condensing undecenoic acid with ethyl hydrogen adipate), the amount of material to be electrolysed is greatly reduced. The development of a successful design of electrolyser[6] has made this method acceptable in production. All stages of the synthesis have been thoroughly worked out and tested in the production of Thibetolide in commercial undertakings[7-9].

However, although these schemes include a simple and elegant method of cyclisation, the starting ω-hydroxy-acids can be prepared only with difficulty and in relatively low yields; in the preparation of Thibetolide, the main difficulty arises from the combination of like as well as of unlike acid residues in the electrochemical cross-condensation.

The composition of the mixture of products formed together with ω-hydroxypentadecanoic ester in the electrolytic cross-condensation of ω-acetoxyundecanoic acid and monoethyl adipate has been thoroughly studied[10].

In the VNIISNDV laboratories several routes from αω-dicarboxylic acids to ω-hydroxyalkanoic acids (*via* the diesters or polyanhydrides) have been tried. Partial catalytic hydrogenation of the diesters of αω-dicarboxylic acids gives the ω-hydroxy-carboxylic ester and the corresponding diol[11] in about equal amounts. The conditions for the formation of glycols and hydroxy-acids in the hydrogenation of aliphatic dicarboxylic acids and their esters have been studied by other workers[12]. An investigation into the catalytic dehydrogenation of αω-diols in the presence of copper–nickel and copper–chromate catalysts has been described[13].

The use of tetrachloroalkanes, formed by the telomerisation of ethylene and carbon tetrachloride

$$n\,CH_2{=}CH_2 + CCl_4 \xrightarrow{\text{initiator}} Cl(CH_2CH_2)_nCCl_3,$$

presents entirely new opportunities for the synthesis of ω-hydroxy-acids and many other products required for the preparation of macrocyclic compounds.

In recent years this process, and also the varied chemical reactions of the tetrachloroalkanes, have been studied in detail in the Laboratory of Organoelementary Synthesis of the USSR Academy of Sciences. This work has led to the development of convenient methods for the preparation of various bifunctional compounds, including ω-hydroxy--acids.

To develop a method of preparing macrocyclic lactones based on tetrachloroalkanes, conditions for the formation of higher tetrachloroalkanes, containing 13–17 carbon atoms, in the telomerisation reaction had to be studied. It has been established[14] that increases in pressure and in the relative concentration of ethylene promote the formation of higher telomerisation products; conditions were so chosen that the telomerisate contained up to 20% of the C_{13}–C_{17} tetrachloroalkane fraction. A flow-type plant has been described for the continuous production of higher tetrachloroalkanes that consistently reproduces the synthetic process under a pressure of less than 150 atm with increased concentrations of ethylene and initiator[15].

The conversion of ααaω-tetrachloroalkanes into ω-hydroxy-acids is achieved by the following simple scheme

$$Cl(CH_2CH_2)_nCCl_3 \xrightarrow{\text{acid hydrolysis}} Cl(CH_2CH_2)_nCOOH \xrightarrow{\text{alkaline hydrolysis}} \rightarrow HO(CH_2CH_2)_nCOOH.$$

These reactions have been studied with various telomers[16].

The following sequence of operations has proved most useful in the development of a method for the production of macrocyclic lactones from tetrachloroalkanes. A broad C_{13}–C_{17} telomer fraction is separated and converted *via* the corresponding chloro- and hydroxy-acids into a mixture of lactones, which can then be easily fractionated to give individual macrocyclic lactones[17,18]. Because ααaω-tetrachloroalkanes are unstable at high temperatures in the presence of even slight traces of heavy-metal salts, the separation from the telomerisate of the higher tetrachloroalkane fraction for use in large-scale production is difficult. Under these conditions dehydrochlorination occurs, leading to the formation of trichloroalkenes, which readily form resins:

$$Cl(CH_2CH_2)_nCCl_3 \xrightarrow{-HCl} Cl(CH_2CH_2)_{n-1}CH_2CH{=}CCl_2.$$

This problem has been solved in several ways. For example, good results have been obtained by first separating the tetrachloroalkane mixture by extraction with polar solvents, and also by distilling off lighter fractions on an ordinary column apparatus, with subsequent separation of higher fractions by hydrovacuum distillation or by fractional distillation with glycerol or ethylene glycol vapour under reduced pressure.

ααaω-Tetrachloroalkanes may also be converted into ω-chloro-acids by the action of concentrated sulphuric[19], nitric[20,21], or perchloric[22] acid. The C_{13}–C_{17} telomers are most conveniently hydrolysed by heating with nitric acid, first to 40–45°, and then at 70°. The yield of chloro--acid mixture is about 89%, calculated on the C_{15} acid[17]. The ω-chloro-acids are converted into ω-hydroxy-acids in 83% yield by the action of aqueous alkali at 6–7 atm.[17] Hydroxy-acids are successfully lactonised *via* the intermediate polyester, which is then subjected to thermal depolymerisation in the presence of an alkaline catalyst[23]:

$$x\,HO(CH_2CH_2)_nCOOH \xrightarrow{-(x-1)H_2O} H[O(CH_2CH_2)_nCO]_xOH \rightarrow x\,(CH_2CH_2)_n{-}CO.$$
(O)

The polyester is readily obtained in quantitative yield by heating the hydroxy-acid (or mixture of hydroxy-acids) to 200–220° under slightly reduced pressure; this is lactonised without purification by heating with glycerol. The lactone formed is distilled off in glycerol vapour.

The formation of lactone from polyester may be considered as an unusual intramolecular transesterification

$$H\{-O(CH_2CH_2)_nCO\ldots[-O(CH_2CH_2)_nCO-]_x\ldots O(CH_2CH_2)_nCO-\}OH \rightarrow$$
$$\rightarrow H\{-O(CH_2CH_2)_nCO\ldots[-O(CH_2CH_2)_nCO-]_{x-1}\ldots O(CH_2CH_2)_nCO-\}OH + \underset{\llcorner\!\!-O-\!\!\lrcorner}{+(CH_2CH_2)_nCO}.$$

Glycerol in the reaction mixture facilitates removal of the lactone formed and promotes lactonisation. The intramolecular transesterification appears to be coupled with transesterification of the polyester by glycerol, which leads to the formation of glycerides of differing molecular weight; in turn these undergo cleavage to form the lactone. The addition of an alkaline reagent evidently promotes transesterification[23]. The yield of lactones is 70–75%, based on the initial mixture of hydroxy-acids.

ω-Chloroalkanoic acids may also be converted into lactones without the hydroxy-acid stage: treatment with alkali yields directly a polyester of the structure $Cl(CH_2CH_2)_nCO[O(CH_2CH_2)_nCO]_xOK$,[24,25] which is then converted into a lactone (or mixture of lactones if a mixture of chloro-acids has been used) by the method described above for the lactonisation of polyesters obtained from hydroxy-acids.

The rational use of telomers derived from ethylene and carbon tetrachloride, other than the C_{13}–C_{17} compounds, makes the production of macrocyclic lactones still more useful. One of the most promising ways of using tetrachloroalkanes as starting materials is the production of oxa-lactones with multiple links. Some of the macrocyclic oxa-lactones, which differ from the macrocyclic lactones by having one $-CH_2-$ link replaced by an $-O-$ link, are of undoubted interest in perfumery as musk preparations with a characteristic variation in odour.

Virtually no macrocyclic oxa-lactones have hitherto been synthesised on the industrial scale, because of the inaccessibility of the ω-halogeno-acids. There are references to the use in perfumery practice only of those oxa-lactones that can be obtained from a halogen derivative of undecenoic acid, for example 12-oxatetradecanolactone, synthesised by the reaction of 11-bromoundecanoic acid with ethylene glycol, and 12-oxahexadecanolactone, obtained from bromoundecanoic acid and tetramethylene glycol.

Now that various ω-halogeno-acids have become readily available, the production of perfumery materials from oxa-lactones of general formula

$$\underset{\llcorner\!\!-O-\!\!\lrcorner}{(CH_2)_mO(CH_2CH_2)_nC=O},$$

presents many possibilities.

A number of oxa-lactones have been synthesised by the reaction of C_5, C_7, C_9, and C_{11} chloro-acids with ethylene glycol[17], butanediol[26], pentanediol[26], hexanediol[17], nonanediol[17] and decanediol[17], the oxa-hydroxy-acid formed being subsequently coverted into the oxa-lactone *via* the polyester:

$$HO(CH_2)_mONa + Cl(CH_2CH_2)_nCOOH \rightarrow$$
$$\rightarrow HO(CH_2)_mO(CH_2CH_2)_nCOOH \xrightarrow{\text{lactonisation}} \underset{\llcorner\!\!-O-\!\!\lrcorner}{(CH_2)_mO(CH_2CH_2)_nC=O}.$$

Preliminary conclusions have been reached about the dependence of odour on structure in this group of perfumery materials[17,26]. The odour of oxa-lactones containing 15 carbon atoms in the ring is close to that of pentadecanolactone, while C_{16} oxa-lactones have an odour similar to that of hexadecanolactone. The introduction of an oxa-link into the molecule of a macrocyclic lactone leads to some loss of odour, and when two oxa-links are introduced the odour disappears almost completely. The odour of oxa-lactones in which the oxa-link is close to the alkoxycarbonyl group is less intense than the odour of those in which the link is more remote.

A number of oxa-lactones have been tested for persistence with respect to rate of evaporation. 10- and 12-Oxahexadecanolactone are highly valued for their properties; they have a musk odour to that of Thibetolide, but are more persistent[26,27]. References to the good properties of 12-oxahexadecanolactone have also appeared in foreign [non-Russian] papers[28,29]. An American patent[30] gives a method for the preparation of 12-oxatetradecanolactone from undecenoic acid and ethylene glycol.

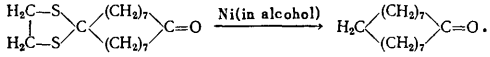
A method recently proposed[31] for the preparation of higher αω-diols by degradative hydrogenation of the polyesters of the corresponding ω-hydroxy-acids:

$$x\,HO(CH_2)_nCOOH \rightarrow H[O(CH_2)_nCO]_xOH \xrightarrow{+2xH_2} x\,HO(CH_2)_{n+1}OH + H_2O,$$

greatly extends the possibilities for the production of various oxa-lactones.

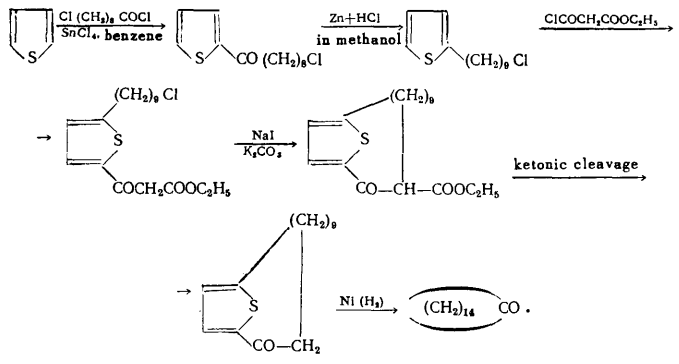
Some papers on the synthesis of macrocyclic compounds are exploratory and have not found practical application.

Blomquist *et al.*[32] have synthesised the musk preparations cyclohexadecanone and cyclooctadecanone by heating the monoethylene dithioketals of the corresponding diketones with Raney nickel in alcohol, for example

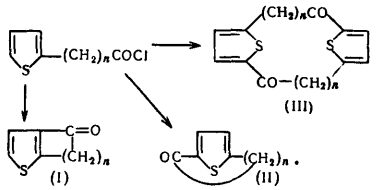


A similar reaction has been described by Cram[33].

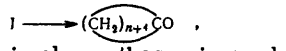
An interesting method has been described[34,35] for the preparation of cyclopentadecanone, which is the main carrier of the musk odour in the product known as Exaltone, isolated from the glands of the musk-rat. It was synthesised by the scheme



In very interesting work, Gol'dfarb *et al.*[36-40] have studied conditions for the formation of intramolecular acylation products (I) and (II) and intermolecular cyclisation products (III) from ω-thien-2'-ylalkanoyl chlorides according to the schemes



Detailed development of methods for the preparation of new ketones of type (I) containing the thiophen ring[37-39,41,42] and also methods for their reductive desulphurisation[37]

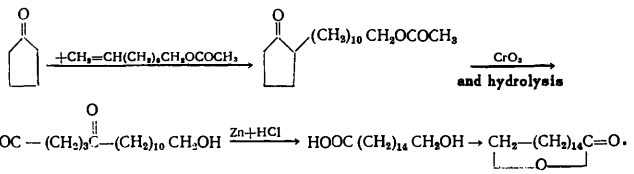


has led to relatively simple syntheses in good yield of a number of useful macrocyclic ketones with a musk odour, including cyclopentadecanone (exaltone), cyclohexadecanone, and cycloheptadecanone (dihydrocivetone). The desulphurisation of thiophen systems for the preparation of intermediates in the synthesis of macrocyclic compounds has been described in other papers[43-47].

Attention has been directed[48] to wastes from cork oak and Amur cork woods as possible additional sources for the preparation of perfumery materials. These contain phloionic acid $HOOC(CH_2)_7(CHOH)_2(CH_2)_7COOH$, which can be converted into macrocyclic compounds.

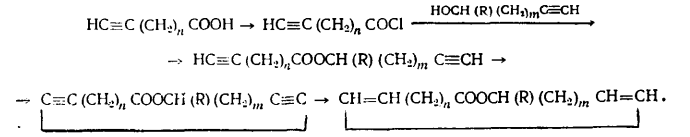
Preobrazhenskii and his coworkers[49] have achieved a multistage synthesis of 3-methylhexadecane-1,16-dioic acid, an intermediate in the preparation of muscone. Some new schemes have been proposed for the synthesis of Exaltolide (Thibetolide)[50,51], ambrettolide[52], exaltone[50,51,53], civetone[54], and dihydrocivetone[51,53,54].

New methods of synthesising dicarboxylic acids[55] and hydroxy-acids[56] which may be converted into macrocyclic compounds are based on the addition of cyclopentanone and cyclohexanone to undecenoic acid[55] or undecenyl acetate[56] in the presence of t-butyl peroxide. Thus, dihydroambrettolide has been obtained[56] in the following way

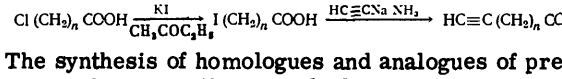


The importance of studying compounds with large and medium rings has been emphasised in a review by Gol'dfarb and Belen'kii[57]. Very interesting work has recently been reported on the preparation and properties of macrocyclic compounds containing aromatic rings[58] and conjugated double[59], or double and triple[60,61], bonds; a review has been published[62] on polymethylene rings containing an acetylenic bond.

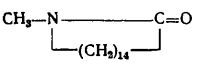
A method has been developed for the preparation of diyne and diene macrocyclic lactones according to the scheme[63-65]



Hydrogenation of the unsaturated macrocyclic lactones, which are practically odourless, gave the corresponding saturated cyclic compounds. In a similar way, saturated macrocyclic ketones were obtained *via* diacetylenic ketones[66]. The ω-acetylenic acids used as starting materials in these new syntheses were prepared from the readily accessible ω-chloro-carboxylic acids[64]:

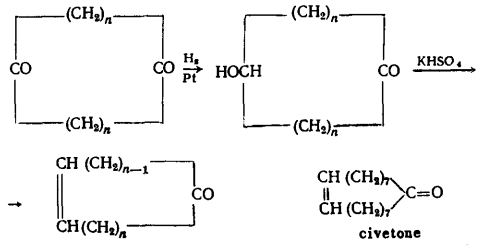


The synthesis of homologues and analogues of previously known musk preparations are dealt with in a number of papers. The recently synthesised 2-methyl-2-azacyclohexadecanone



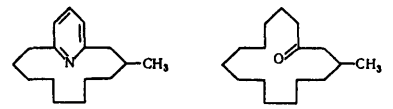
[other] macrocyclic *N*-methylamides, and macrocyclic *N*-methylurethanes, in which nitrogen is a component of the many-membered ring, have been described as compounds with a musklike odour[67,68]. These examples again emphasise that the odour of a compound is determined not only by the presence of certain groups of atoms, but also by the structure of the molecule as a whole.

Cyclohexadec-8-en-1-one (IV) and cyclooctadec-9-en-1-one (V), homologues of civetone with an intense musk odour, have been synthesised[69,70] by partial hydrogenation of cyclohexadecane-1,9-dione and cyclooctadecane-1,10-dione respectively, followed by dehydration of the hydroxy-ketones obtained:



(IV) $n=7$
(V) $n=8$

Ruzicka[71] isolated a compound $C_{16}H_{25}N$ from the glands of the musk-deer (*Moschus moschiferus*), which he termed "muscopyridine". Recently its structure has been determined and confirmed by synthesis[72]. This compound shows some structural similarity to the known macrocyclic ketone muscone, which also occurs in the glands of some musk animals.



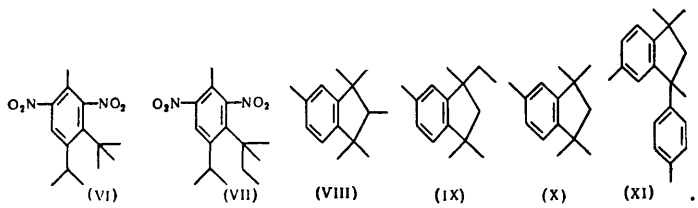
muscopyridine ($C_{16}H_{25}N$) muscone ($C_{16}H_{30}O$)

II. MUSK PREPARATIONS OF THE AROMATIC SERIES — POLYALKYLINDANES, ETC.

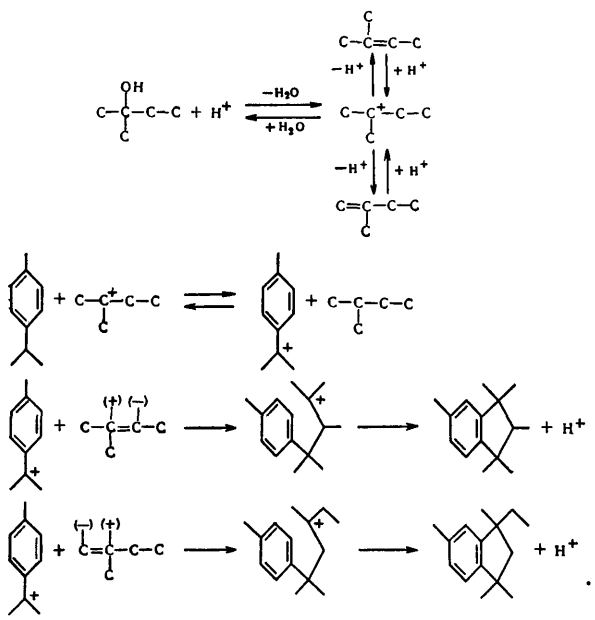
A study of the alkylation of *p*-cymene led to the discovery of an essentially new class of perfumery compounds with a musk odour. Until recently it was thought that the action of a tertiary alcohol or a branched olefin on *p*-cymene in the presence of a catalyst[73-77] resulted in nuclear alkylation. Thus, the fragrant compound prepared by reaction of t-butyl alcohol with *p*-cymene followed by

nitration of the alkylated product was described as dinitro--t-butyl-*p*-cymene (VI)[76,77]. The structure (VII) was assigned to the homologue synthesised some time later by alkylating *p*-cymene with 2-methylbutan-2-ol.[74]

It has been established that in these reactions *p*-cymene behaves in a different way from other aromatic hydrocarbons. The reaction in the presence of concentrated sulphuric acid of tertiary or secondary alcohols having a tertiary carbon atom gives a mixture of indane hydrocarbons as the main product, not products alkylated in the aromatic nucleus[78-82]. Thus, alkylation of *p*-cymene with 2-methylbutan-2-ol gives 1,1,2,3,3,5-hexamethylindane (VIII) (41%), 1-ethyl-1,3,3,6-tetramethylindane (IX) (23%), 1,1,3,3,5-pentamethylindane (X) (12%), a substituted indane $C_{16}H_{24}$ (structure not established), and 1,1,3,5-tetramethyl--3-*p*-tolylindane (XI)[78]. The stoichiometric equation for the main reaction may be expressed: 1 mole of *p*-cymene + + 2 moles of 2-methylbutan-2-ol = 1 mole of C_{15} indanes + + 1 mole of isopentane + 2 moles of H_2O.



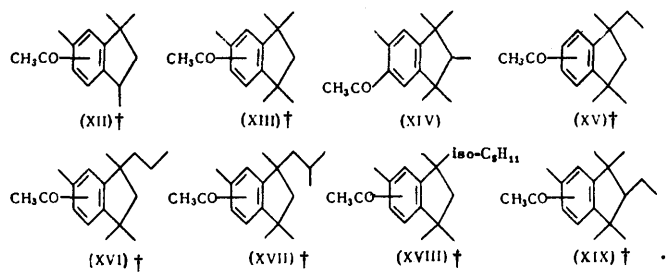
The following mechanism has been proposed to explain the formation of the main products of this reaction[78,79]



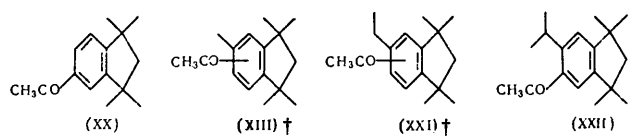
Side-reactions with elimination and migration of the methyl group give C_{14} and C_{16} indanes. *p*-Ethylcumene and *p*-t-butylcumene also tend to form indane derivatives in similar alkylations[79].

A large number of derivatives of different kinds have been synthesised from the polyalkylindanes obtained, and some relationships between structure and odour have been established. Weber *et al.*[78,79,83] found that acetylpolyalkylindanes have a musk odour when there are two pairs of *geminal* methyl groups on the carbon atoms adjacent to the benzene ring. Most of these indanes have 1-3 alkyl groups in the benzene nucleus; an additional 6-methyl group weakens the musk odour. According to Beets *et al.*[84], the presence of an acyl group and two tertiary or quaternary carbon atoms attached to the benzene nucleus is the minimum condition for the presence of a musk odour in indane derivatives. These tertiary or quaternary carbon atoms may be present in the non-aromatic ring, or one of them may be introduced as an independent alkyl group. Compounds with an acyl and two quaternary groups have a strong musk odour.

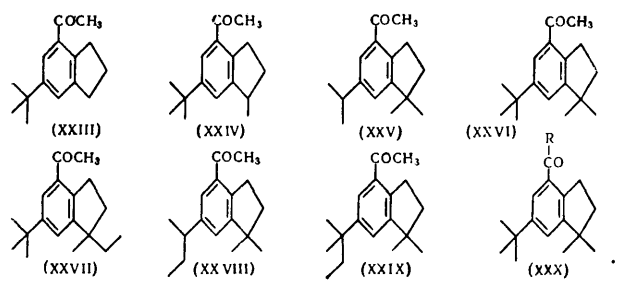
Some special odour-structure relationships of polyalkylindane derivatives may be traced in the following compounds



Compound (XII) is odourless[78]; according to one report[80], compound (XIII) has a weak musk odour, but according to other workers[78,82] it has a musk-wood odour weaker than that of (XIV); (XIV) has a strong musk odour[78-82], and the odour of (XV) does not differ in character but is much weaker[78,82]. Compounds (XVI)-(XVIII) are completely odourless[59], and (XIX) has a musk odour[79].



In the series (XX), (XIII), (XXI), (XXII), which contain the same non-aromatic ring, the first two members have a weak musk odour[78-80,82,84]; (XXI) has been described as a compound with a musk odour; and its homologue (XXII), with an isopropyl group in the benzene ring, is odourless[79].



Of the compounds (XXIII)-(XXIX) with an acetyl group on the same carbon atom of the benzene ring, (XXIII)[84] is

† Later work indicates that in all these compounds the acetyl group is in the same position as in compound (XIV), the structure of which has been established[85].

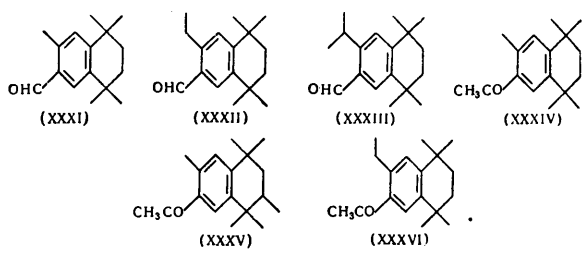
odourless, its homologue (XXIV) has a very weak musk-type odour[84], the ketones (XXV)–(XXVII) have been described as compounds with a strong musk odour[84,86–88], and compounds (XXVIII) and (XXIX)[84] have a weak musk odour.

Among compounds of general formula (XXX) that have been synthesised, the aldehyde (R = H) has a very strong musk odour[84], and the acetyl derivative (R = CH_3) has a strong musk odour (see above), which gradually becomes weaker as the molecular weight of the ketone increases (R = C_2H_5; R = C_3H_7).[84,86]

It will be noted that, both in the example given above and in the other cases described, the aldehydes of the polyalkylindane series have a stronger musk odour than the corresponding methyl ketones[83,84]

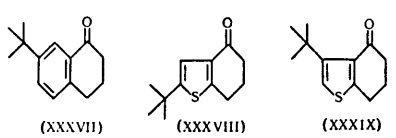
Some of the new polyalkylindane derivatives have found applications in the perfumery industry. Thus, 5-acetyl-1,1,2,3,3,6-hexamethylindane (XIV), provisionally termed Phantolid[82,89,90], has become known as a perfumery material with a persistent musk odour. Special mention has been made in the perfumery journals of the high odoriferous qualities of the indane derivatives (XXVI), (XXIX), and (XXX) with R = C_2H_5,[86,87,91,92] and they have been recommended for use in compositions for perfumes, eau de Cologne, scented soap, powders, etc.

Polyalkyltetralin derivatives with a musk odour, and similar in structure to the above compounds of the indane series, are described in a number of reports, mainly from the patent literature. 1,2,3,4-Tetrahydro-1,1,4,4-tetramethylnaphth-6-aldehydes containing an extra methyl or an ethyl group at position 7 — (XXXI) and (XXXII) — have a strong musk odour; the corresponding 7-isoproyl derivative (XXXIII)[93,94] has a weaker musk-type odour.

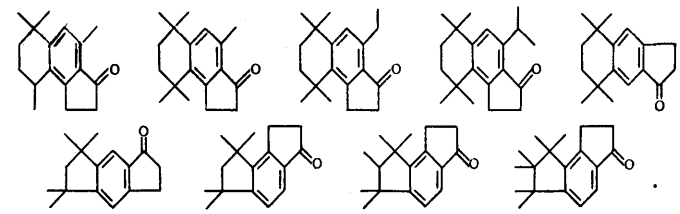


Ketones of the substituted alkyltetralin group that have been described as compounds with a musk odour include the homologues of 6-acetyl-1,2,3,4-tetrahydro-1,1,4,4-tetramethylnaphthalene containing 7-methyl (XXXIV)[95], 3,7-dimethyl (XXXV)[96], and 7-ethyl (XXXVI) groups, the last of these compounds being used in perfumery under the name Versalide[97,98].

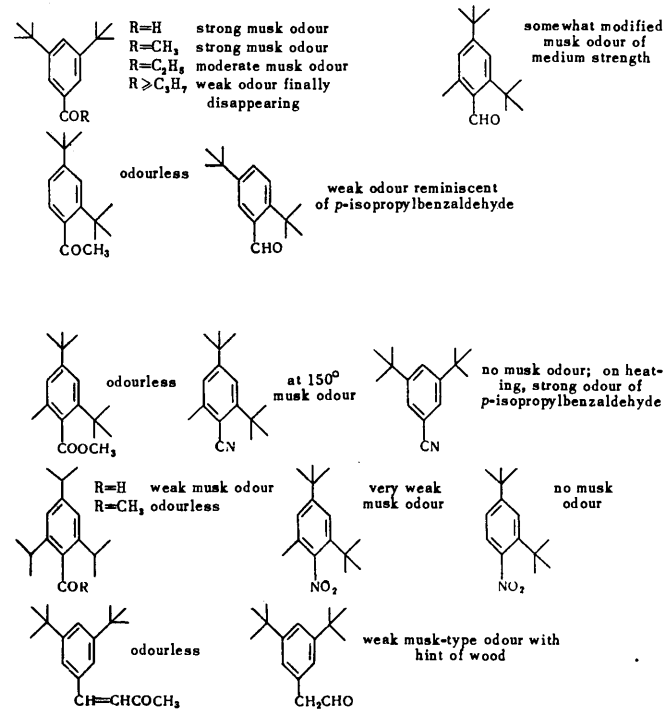
Buu-Hoi and other chemists have described 7-t-butyltetral-1-one (XXXVII) as a compound with the odour of burning sandalwood[99,100]. For comparison, its isologues 2- and 3-t-butyl-4,5,6,7-tetrahydro-4-oxobenzo[*b*]thiophen (XXXVIII) and (XXXIX)[101] have been synthesised; (XXXVIII) is found to have the characteristic odour of burning sandalwood, but the odour of (XXXIX) is less interesting.



In recent years compounds with a musk odour belonging to more complex fused systems have become known. Patents have been obtained for a number of polyalkylhexahydrocyclopentanaphthalenes[102] and for polyalkylhydroindacene derivatives[103], the formulae of which are given below. It is noteworthy that compounds of such high molecular weight (18–20 carbon atoms per molecule) should have an odour; these products are perhaps the "heaviest" known perfumery materials.



In an investigation[104] to elucidate the relationship between the non-aromatic indane ring and the presence of a musk odour, various benzene derivatives were synthesised, and some correlations were found between structure and the character and strength of odour. These products included benzene derivatives without a nitro-group that had a musk odour. Up to now only a few representatives of this group of musk preparation[1,105] have been known. The following are the formulae and characteristic odours of the compounds prepared in this work



From a comparison of the odour of these benzene derivatives with compounds of the indane series, Beets concluded that the non-aromatic indane ring is not essential for the presence of odour. He considered that the benzene nucleus, with bulky groups (*e.g.* t-butyl) and also aldehyde or ketone substituents, preferably in a sterically unhindered position, is the carrier of the musk odour. Beets observed that compounds in which the carbonyl group is

sterically hindered to such a degree that it does not react with carbonyl-group reagents have no musk odour, unlike their isomers with a more "accessible" carbonyl group.

Work on the chemistry of the "nitro-musks" that deserves mention included an investigation into the separate stages of the preparation of musk xylene[106] and a new synthesis of 4-bromo-5-t-butyl-2,6-dinitro-*m*-xylene[107] previously described by Carpenter.

III. OTHER PERFUMERY MATERIALS

Improvements in the preparation of benzyl and phenethyl alcohols and their derivatives continue to attract attention. An industrial method has been described for obtaining benzyl alcohol by hydrolysing benzyl chloride with sodium carbonate solution, and also a method for esterifying benzyl alcohol with acetic acid in the presence of sulphuric acid to give an ester of high perfumery quality[108]. Another paper recommends that benzyl alcohol should be esterified by carboxylic acids (formic, acetic, and some others) in chloroform with chlorosulphuric acid as catalyst[109]. A good yield (86%) of ester was obtained from benzyl alcohol and acetic acid, the water formed being distilled off with toluene vapour[110]. New work has also been described on the preparation of benzyl acetate from benzyl chloride and sodium acetate[111].

A considerable part of the work done to develop industrial methods for the preparation of phenethyl alcohol has been devoted to the study of separate stages in its synthesis from styrene *via* the halogenohydrin and the oxide

$$C_6H_5CH{=}CH_2 \rightarrow C_6H_5CH(OH)CH_2Hal \rightarrow C_6H_5{-}CH{-}CH_2 \rightarrow C_6H_5CH_2CH_2OH.$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \backslash O /$$

Apart from a number of patents obtained in different countries that deal mainly with the catalytic hydrogenation of styrene oxide[112–115], the process as a whole has been thoroughly examined by Beets[116], who points out that this method, which gives phenethyl alcohol of high purity, appears to have been adopted on an industrial scale in the U. S. A. The high quality of the 2-phenylethanol obtained from styrene has recently been confirmed by Soviet workers[117]. The reduction of a number of oxides, including styrene oxide, with lithium tetrahydroaluminate has been described[118].

The preparation of 2-phenylethanol from phenylacetic ester has been described in two recent papers: Daniewski[119] somewhat modified the well-known Bouveault–Blanc‡ reduction of phenylacetic ester, and Bag and Bliznyak[121] obtained good results in the catalytic hydrogenation of this ester with a copper–calcium catalyst§ (at 165–170° and an initial pressure of 200 atm); alcohol of high purity was obtained in 60% yield, based on the ester consumed.

Phenethyl alcohol has been prepared from benzene and ethylene oxide by the Friedel–Crafts reaction[123]. The results have been reported of an investigation into the purification of phenylethanol by vaporised solvents in an injector column[124]. Shutikova and Cherkaev[125] have described the 2-methylation of 2-phenylethanol and 2-cyclohexylethanol, and have reported on the perfumery properties of the products (2-phenylpropanol and 2-cyclohexylpropanol) and also of the corresponding aldehydes.

3-Phenylpropanol has been prepared by two methods, by the reaction of benzylmagnesium chloride with ethylene oxide in ether, and by the reduction of ethyl cinnamate with sodium and pentanol in toluene[126]. These methods are, however, less suitable for industrial use than the method worked out a few years ago at VNIISNDV for its preparation from styrene[127].

Several papers describe the preparation of cinnamyl alcohol by the reduction of cinnamaldehyde. Two variants of the reduction with aluminium isopropoxide[128] have been developed, and the effect of adding aluminium halide alkoxides in this reaction has been studied[129]. Several carbonyl compounds, including cinnamaldehyde, were reduced with a mixture of aluminium isopropoxide and $ClAl[OCH(CH_3)_2]_2$, cinnamyl alcohol being obtained in 92% yield. The alcohol has also been obtained in the same yield (90–92%) by a method in which less the usual amount of aluminium benzyloxide was used[130].

Gorshkov and Freidlin have made a comprehensive study of the reduction of a number of unsaturated carbonyl compounds, including cinnamaldehyde, on zinc catalysts obtained by leaching out Zn–Al and Zn–Cu–Al alloys. They find that selective reduction of the ethylenic bond or of the carbonyl group depends on their relative positions[131]. Polish workers have proposed a new method for the preparation of cinnamyl alcohol from styrene *via* pentylzinc chloride and the corresponding acetate[132].

Several papers deal with the preparation of alcohols of interest in the perfumery industry. Japanese workers have described[133] the hydrogenation of aliphatic acids, isolated from coconut oil, to the corresponding alcohols in the presence of a mixed $CuSO_4$–$Na_2Cr_2O_7$ catalyst and aqueous ammonia. They consider that hydrogenation of the acid itself occurs only in the initial stage; the alcohol formed then esterifies the acid, and the ester is now hydrogenated to the alcohol. Indian workers have suggested reducing esters to the corresponding alcohols by the action of aluminium amalgam in alcohol; the method is said to have advantages in work with small quantities[134]. Sladkov *et al.*[135], using 2-methylpent-1-ene and 2-ethylhex-1-ene, have made an interesting study of the Ziegler reaction for the conversion of olefins into alcohols *via* organoaluminium compounds

$$6RCH{:}CH_2 + 2Al + 3H_2 \rightarrow 2(RCH_2CH_2)_3Al,$$
$$2(RCH_2CH_2)_3Al + 3O_2 \rightarrow 2(RCH_2CH_2O)_3Al,$$
$$(RCH_2CH_2O)_3Al + 3H_2O \rightarrow 3RCH_2CH_2OH + Al(OH)_3.$$

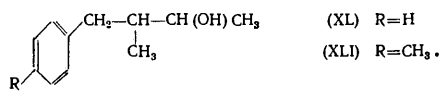
They point out the relative simplicity of this method and the good yield of alcohols obtained (60–65% of theoretical). This reaction was also used for the preparation of 2-phenylpropanol in 55% yield, based on the initial methylstyrene[136]. A group of Soviet workers[137] have described the preparation of 2-phenylpropanol by the reaction of *α*-methylstyrene with isobutylaluminium followed by oxidation with air of the 2-phenylpropylaluminium formed.

According to Weissenborn[138], 3-methyl-4-phenylbutan-2-ol (XL) and 3-methyl-4-*p*-tolylbutan-2-ol (XLI), prepared by the condensation of benzaldehyde and *p*-tolualdehyde with ethyl methyl ketone in acid medium, followed

‡ Filipescu and Manisor[120] recommend that the Bouveault–Blanc reduction of esters should be carried out in aromatic hydrocarbons with sodium and such alcohols as cyclohexanol, methylcyclohexanol, pentanols, etc.

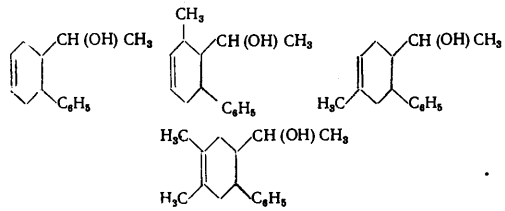
§ According to a patent[122], high yields of aromatic alcohols (up to 95% and above) are obtained in the hydrogenation of esters under pressure in the presence of copper chromite.

by reduction of the unsaturated ketone, have an odour similar to that of linalool.



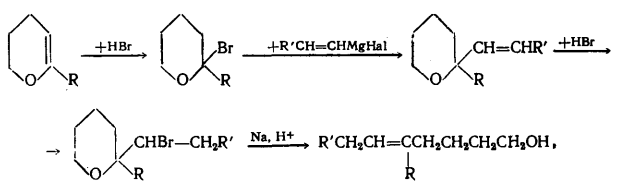
(XL) R=H
(XLI) R=CH$_3$.

A floral odour has been noted[139] in secondary alcohols obtained by the reaction of methylmagnesium iodide with 2-formyl-1,2,3,6-tetrahydrobiphenyl and its homologues, which in turn are obtained by diene synthesis from cinnamaldehyde and the corresponding diene hydrocarbons



An odour close to that of methyl oct-2-ynoate (Folione) has been noted in oct-2-yn-1-ol, obtained by condensing hept-1-yne with formaldehyde[140].

The method developed by Normant for carrying out Grignard syntheses with organomagnesium compounds containing a vinyl-type radical[142] has presented more opportunities for the synthesis of various unsaturated alcohols. Thus, various ethylenic aliphatic secondary and tertiary alcohols[142,143] have been obtained by the reaction of vinylmagnesium bromide, and also its alkyl-substituted derivatives, with saturated aliphatic aldehydes and ketones; analogous reactions with unsaturated carbonyl compounds and esters have led to diethylenic and polyethylenic alcohols[144,145]. Condensation of vinylmagnesium halides and their substituted derivatives with dihydropyran and dihydrofuran hydrobromides gives 2-alkenyltetrahydropyrans and 2-alkenyltetrahydrofurans respectively, which are then converted into δ- and γ-unsaturated primary alcohols[146]

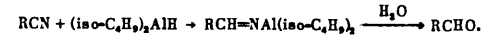


Heptenols and octenols have been synthesised from isohexene and isoheptene hydrocarbons (obtained by the polymerisation of simple olefins), by condensing the latter with formaldehyde (Prins reaction). Under certain conditions the yield of unsaturated primary alcohols reaches 80 wt. %.[147]

Much work has recently been done in the search for new and improved methods for preparing phenylacetaldehyde, cinnamaldehyde, α-p-isopropylbenzylpropionaldehyde, and their homologues and analogues.

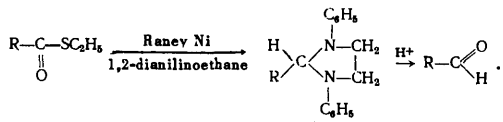
The use of aluminium or iron oxide[148] and of activated aluminium oxide[149] has been proposed for the conversion of styrene oxide into phenylacetaldehyde; when the isomerisation is conducted in an inert gas at 170°, an almost quantitative yield is obtained[149]. Styrene[150] has been used as starting material in the synthesis of cinnamaldehyde: the styrene is chloromethylated to give cinnamyl chloride, which is then subjected to the Sommelet reaction; however, the yield is low. The Sommelet reaction has recently been used[151] for converting 2,4,5-triisopropylbenzyl chloride into the corresponding aldehyde, which had previously been described as a compound with a musk-type odour[105]. Cinnamaldehyde[152] and triisopropylbenzaldehyde[153] have recently been obtained from the corresponding halogeno--derivatives by Kröhnke's method.

Phenylacetaldehyde can be prepared in yields up to 90%[154,155] by the electrolytic oxidation of cyclooctatetraene[156-159]. Zakharkin and Khorlina[160] have prepared phenylacetaldehyde, anisaldehyde, and some other aldehydes by reducing the nitriles with diisobutylaluminium hydride:



The yield of phenylacetaldehyde reaches 86%, that of aubépine (anisaldehyde) 88%.

A new method of preparing phenylacetaldehyde, β-phenylpropionaldehyde, and other aromatic and aliphatic aldehydes by the reduction of carbothiolic esters with Raney nickel has been described[161]. To prevent further reduction of the aldehyde, it is combined with 1,2-dianilinoethane; the compound thus formed is easily decomposed by mineral acids:



This method gives yields of 79%, 84%, and 80% respectively of phenylacetaldehyde, β-phenylpropionaldehyde, and benzaldehyde, calculated on the initial carbothiolates.

New patents have been obtained for a method of stabilising phenylacetaldehyde as its trimer[162,163], which can be decomposed to give the free aldehyde[164].

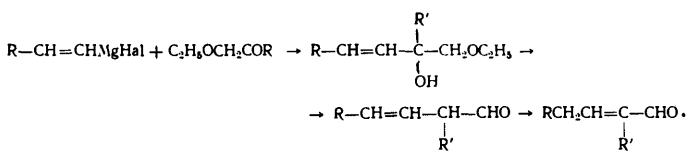
The preparation of aliphatic ketones by pyrolysis of manganese salts of the acids has been studied, as well as the preparation of aldehydes by pyrolysis of manganese formate and a manganese salt of the carboxylic acid. In the synthesis of ketones this method has advantages over the classical Piria reaction (pyrolysis of calcium salts); the yield of aldehydes is generally low, however, but C_7 and C_8 aldehydes can be prepared with good results[165].

A method has been described for the preparation of normal C_{10}, C_{12}, and C_{14} aldehydes by oxidation of the alcohols with selenium dioxide[166]. Dodecanal has been obtained by dehydrating dodecyl alcohol on a copper chromite catalyst[167]; and undecanal and dodecanal have been synthesised from the corresponding bromides and 2-nitropropane in the presence of alcoholic alkali[168].

Conditions for increasing the yield of heptanal and undecenoic acid in the pyrolysis of castor oil have been described in a patent[169].

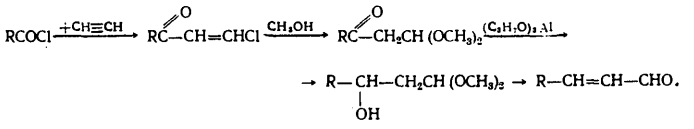
Normant[170] has proposed a method for the preparation of $\alpha\beta$-unsaturated aliphatic aldehydes in which ethoxy--ketones of the type $RCOCH_2OC_2H_5$ react with 1-substituted

vinylmagnesium halides, and the resulting 1-ethoxybut-3--en-2-ols are decomposed with formic acid:



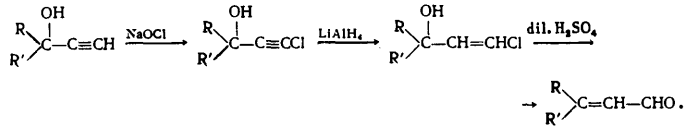
Aldehydes obtained by this scheme include 2-propylidenenonanal (R = CH_3, R′ = C_7H_{15}) with a floral odour, and 2-ethylidenenonanal (R = H, R′ = C_7H_{15}) with a lemon odour.

Two new methods of synthesising $\alpha\beta$-unsaturated aldehydes have been reported. Dec-2-enal, octadec-2-enal, and some other aldehydes of similar structure are prepared by the scheme[171]



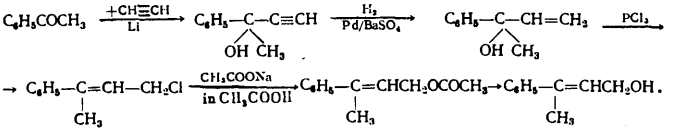
The odour characteristics of these compounds are not mentioned.

Substituted ethylcarbinols are used as starting materials in another method[172]:



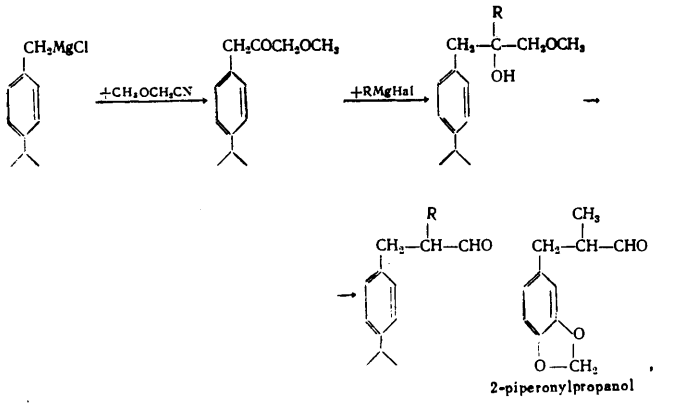
The aldehydes were not separated in the pure state but were characterised as their semicarbazones.

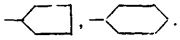
Homologues and analogues of well-known perfumery materials are described in a number of other papers. Thus, β-methylcinnamaldehyde, which has an odour similar to that of cinnamaldehyde, has been obtained[173] by reduction of ethyl β-methylcinnamate to the corresponding alcohol, which is then oxidised to the aldehyde. A year later, γ-methylcinnamyl alcohol, from which this aldehyde can readily be obtained, was synthesised from acetophenone according to the scheme[174]



The next homologue of jasminaldehyde, with a methyl group in the nucleus, p-methyl-α-pentylcinnamaldehyde[175], has an odour close to that of jasminaldehyde but coarser.

Cyclamenaldehyde (α-p-isopropylbenzylpropionaldehyde) and several of its homologues and analogues with different alkyl groups in the α position to the carbonyl group have been synthesised by the new scheme[176,177]



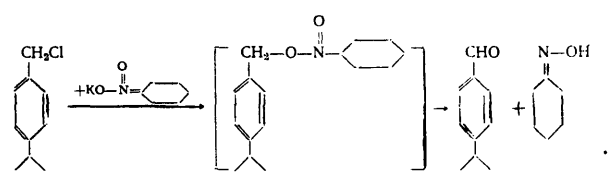
where R = CH_3 (cyclamenaldehyde), C_2H_5, n-C_3H_7, iso-C_3H_7, iso-C_4H_9, iso-C_5H_{11},  .

The odour of these compounds is inferior in strength and quality to that of cyclamenaldehyde itself; 2-p-isopropylbenzyl-5-methylhexanal (R = iso-C_5H_{11}) is the only one that has been described as a compound of distinctive odour with a musk trend.

A method of synthesis of the new perfumery material 2-piperonylpropanal [α-(3,4-methylenedioxybenzyl)propionaldehyde], an analogue of cyclamenaldehyde, was patented in 1960 [178] and then developed in detail by Laskina and Devitskaya[179]. Its excellent perfumery properties have been noted.

Among other isomers and homologues of cyclamenaldehyde that have been synthesised recently, β-(p-t-butylphenyl)propionaldehyde[180] has a strong odour of lilies, β-p-cumenylbutyraldehyde[181], an agreeable odour, and α-p-methylbenzylbutyraldehyde[182] an odour reminiscent of cyclamenaldehyde. Japanese workers have patented[183] a series of homologues of cyclamenaldehyde that differ from it in having alkyl groups in the α position to the aldehyde group, and also in the *para* position to the propyl chain. In a United States patent[184] the dimethylacetal of 2-benzylpropanal, a lower homologue of cyclamenaldehyde, is recommended for use in perfumery.

Some research was done on the preparation of cyclamenaldehyde itself. A synthesis *via* the substituted acetoacetic ester p-iso-$C_3H_7.C_6H_4.CH_2.C(CH_3)(COCH_3).COOC_2H_5$ has been published: acid cleavage gives α-p-isopropylbenzylpropionic acid, which is then reduced to the aldehyde[185,186]. p-Isopropylbenzyl chloride has been converted[187] into the aldehyde by the action of an alkaline aqueous-alcoholic solution of nitrocyclohexane:



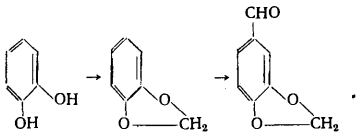
Oxidation of p-isopropylbenzyl chloride followed by condensation with propionaldehyde of the p-isopropylbenz-

aldehyde formed gives *p*-isopropyl-α-methylcinnamaldehyde in 58% yield, calculated on the initial *p*-isopropylbenzyl chloride.

The reduction of *p*-isopropyl-α-methylcinnamaldehyde to cyclamenaldehyde in the presence of Raney Ni–W-5 (from an Ni–Al alloy) in methanol[188] has been studied by infrared spectroscopy and gas chromatography. It has been shown that the mixture obtained under these conditions contains ~ 53% of cyclamenaldehyde; *p*-isopropyl-β-methylcinnamyl alcohol and 2-*p*-isopropylbenzylpropanol are formed as by-products. The latter can be converted into cyclamenaldehyde in 60% yield by dehydrogenation at 230–240° and a residual pressure of 28–30 mm in the presence of copper–chromic oxide catalyst with the addition of barium oxide[189].

It has been suggested that in the preparation of cyclamenaldehyde it is useful to hydrogenate *p*-isopropyl-α-methylcinnamaldehyde to 2-*p*-isopropylbenzylpropanol and then convert this to the aldehyde[190].

Workers at VNIISNDV have continued to develop a method for the synthesis of heliotropin (3,4-methylenedioxybenzaldehyde) from catechol. Simplifications have been introduced into separate stages of the synthesis, which was first proposed in 1938 [191]



Until recently the methylenation stage was effected by heating catechol with methylene chloride in alkaline medium under pressure; this was accompanied by the formation of much resin. It has been shown that methylenation can be successfully carried out at ordinary pressures in the presence of sodium iodide in benzyl alcohol[192,193]. To introduce the aldehyde group into the molecule of catechol methylene ether, several variants have been employed of a method for preparing hydroxy-aldehydes containing a free phenolic group which has been widely used, for example in the synthesis of vanillin[194–196].

In another scheme the aldehyde group is introduced directly into the catechol molecule, and the resulting aldehyde converted into the methylene ether[197].

In the production of heliotropin from the essential oil of sassafras, isosafrole, obtained by isomerisation of the safrole contained in the oil, has been oxidised electrolytically[198].

It is natural that new synthetic methods for preparing vanillin and the improvement of existing industrial methods should attract attention. The synthesis of vanillin from salicylic acid in two stages has recently been reported[199]. However, until the results are confirmed it is difficult to evaluate the method.

The so-called chloral method for the preparation of vanillin and vanillal has been improved[200]. When dichloroethane is used as solvent in the formation of 4-hydroxy-3-methoxyphenylglycollic acid (and also the 3-ethoxy-compound), a yield of 80–85% is obtained, based on the initial guaiacol (or guethol); technical chloral hydrate was used in the condensation. It has been proposed that oxidation of the condensation product in the last stage of the synthesis should be carried out with an air spray in the presence of a permanganate catalyst. The total yield of vanillin was 50–55%, calculated on the guaiacol taken.

Comparative results on the preparation of vanillin from guaiacol and formaldehyde with the use of nitrosodimethylaniline (the so-called nitroso-method) or *m*-nitrobenzenesulphonic acid are given in a paper published in 1963 [201].

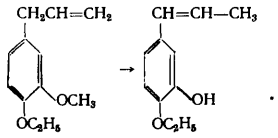
The products of the condensation of guaiacol with formaldehyde have been investigated[202] with the object of preparing 4-hydroxy-3-methoxybenzyl alcohol, a supposed intermediate in the synthesis of vanillin from guaiacol, but the pure alcohol could not be isolated from the reaction mixture

The development of convenient methods for the preparation of guaiacol and guethol from catechol and its mixtures[203–205] extends the range of raw materials available for the synthesis of vanillin and vanillal.

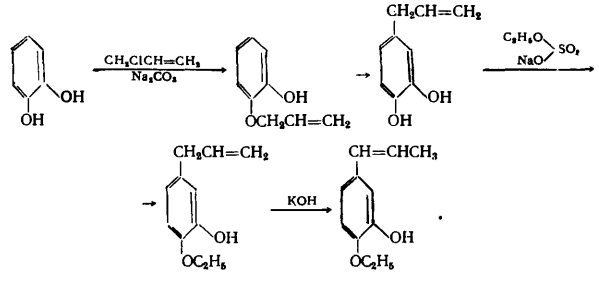
The search has continued for improved conditions for the preparation of vanillin from lignin, its derivatives, or lignin-containing materials; most of these investigations have been reported in the patent literature (reviewed in Ref. 206).

Good results have been obtained in work on the preparation of vanillin by alkaline oxidation of lignosulphonates contained in post-alcohol residues, a waste product of the sulphite–alcohol industry[207–209].

The odour of a series of recently synthesised aromatic aldehydes — analogues of vanillin, vanillal, and heliotropin — has been described[210]. Patents have been obtained[211,212] for the preparation of 2-ethoxy-5-propenylphenol, an interesting perfumery material with the odour of vanilla¶, from the ethyl ether of eugenol, which is subjected to demethylation accompanied by isomerisation of the allyl group to propenyl:

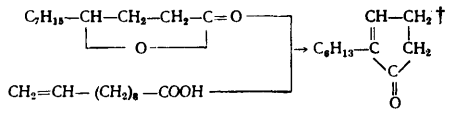


Laskina *et al.* [214] have recently developed the following synthesis of Vanitrope



¶ Marketed by the American firm Shulton Inc. as Vanitrope.[213]

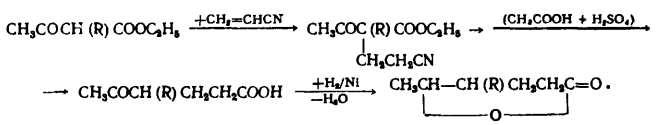
Some new work has been devoted to the preparation of substituted cyclopentenones, a group that includes the interesting perfumery material jasmone (3-methyl-2-pent-2'-enylcyclopent-2-enone), a constituent of the essential oil of jasmin. 2-Hexylcyclopentenone, the so-called dihydrojasmone, has been used in the industry; it is obtained by cyclodehydration of γ-undecanolactone or of undecenoic acid.



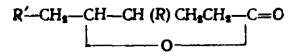
Polyphosphoric acid has recently been proposed for converting γ-lactones [215,216], δ-lactones [217], and unsaturated acids [218,219] into alkylcyclopentenones. High yields have been obtained and new interpretations of the mechanism of reactions of this kind have been put forward.

According to some reports [220], the use of polyphosphoric acid for the preparation of dihydrojasmone itself from undecenoic acid gives the required product in good yield; according to other reports [219], a mixture of isomeric ketones is formed and the yield of dihydrojasmone is low. Comparative results on the preparation of dihydrojasmone from undecanolactone and from undecenoic acid by the action of polyphosphoric acid have been reported [221]. A new synthesis of dihydrojasmone has also been described [222].

Work in recent years on the development of new methods for the preparation of alkyl-substituted γ- and δ-lactones includes the promising synthesis suggested by Belov and Dil'man [223] of γδ-dialkylated δ: lactones; this has been further developed by Belov and Voitsekhovskaya [224,225]:



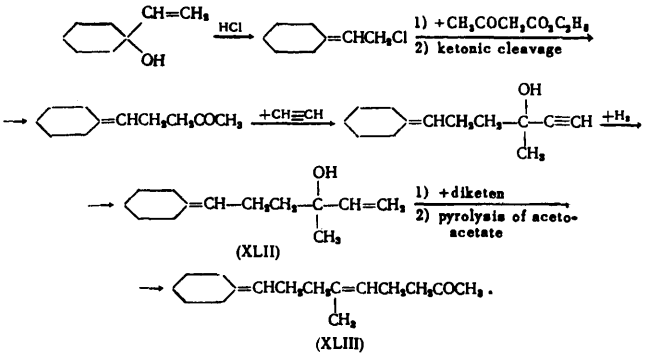
The use in this synthesis of esters of keto-acids $R'CH_2COCH(R)COOC_2H_5$, obtained by ester condensation of esters of aliphatic acids, enables δ-lactones of general formula



to be synthesised relatively easily; new substituted cycloalkenones, analogues of dihydrojasmone, may be obtained from these by cyclodehydration.

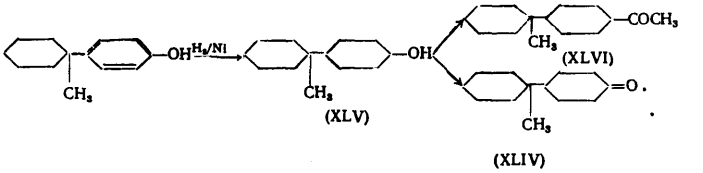
Petrov, Nikishin, and their coworkers [226-228] have recently published detailed papers on the preparation of various alkylated γ- and δ-lactones, several of which may be of interest in perfumery.

Surmatis [229,230] and Kimel [231] have described the preparation of 6-cyclohexylidene-3-methylhex-1-en-3-ol (XLII), which has a musty odour (recommended for conferring an earthy odour on floral compositions), and 9-cyclohexylidene-6-methylnon-5-en-2-one (XLIII), which has been described as a compound of rose fragrance with a fruity shade. These compounds were synthesised from 1-vinylcyclohexanol by the scheme

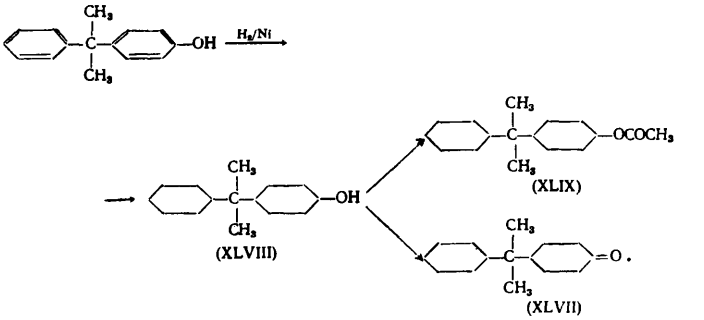


The acetates, propionates, butyrates, and isobutyrates of *cis*- and *trans*-isomers of 4-t-butylcyclohexanol have been found to differ greatly: the odour of the *cis*-isomers is 2–5 times as strong as that of the corresponding *trans*-isomers, and it is also more delicate [232].

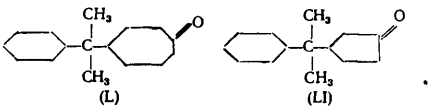
Belov and his coworkers [233] have observed an interesting odour, resembling that of vetiver oil, in the ketone (XLIV); the corresponding alcohol (XLV) has a strong characteristic odour, and its acetate (XLVI) an odour close to that of musterone. These compounds are easily prepared from *p*-1-methylcyclohexylphenol:



The ketone (XLVII), the alcohol (XLVIII), and its acetate (XLIX) have only a weak, uncharacteristic odour, that of the ketone being somewhat stronger. These compounds are prepared by the scheme [234]



Change from a five- to a seven-membered ketonic ring has no material effect on the odour. The ketones (L) and (LI) have the same kind of odour as the ketone (XLVII); the ketone having a five-membered ring possesses the strongest odour [235].



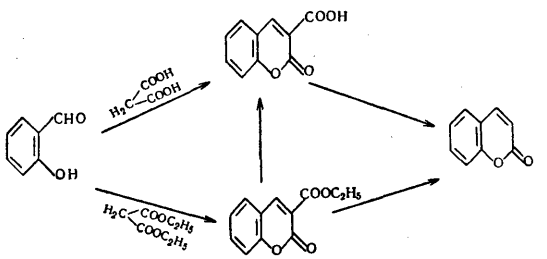
Improvements in the synthesis of isoeugenol from guaiacol *via* its propionate are reported in several publications. The propionate is converted by Fries' rearrangement into

† One of the isomers, which differ in the position of the double bond in the ring, is shown.

4-hydroxy-3-methoxypropiophenone, which is hydrogenated to the corresponding alcohol; the alcohol is then dehydrated to give isoeugenol[236-241]. In work on the direct *C*-allylation of guaiacol *para* to the hydroxy-group, Tsukervanik and Mel'kanovitskaya[242-244] developed a method of preparing eugenol by the interaction of guaiacol and allyl chloride in the presence of a copper catalyst. The yield of the resulting mixture of allylguaiacols is ~29%, based on the allyl chloride taken, or 39% on the guaiacol consumed; the eugenol content of this mixture, determined by infrared spectroscopy[245], is 59%[244].

Allylation in the presence of a copper catalyst has also been used for the preparation of safrole from methylenedioxybenzene[246].

Bratus and Voronin[247-249] have studied the separate stages of the synthesis of coumarin [2-oxochromen] by the Knoevenagel reaction, in which salicylaldehyde is condensed with malonic acid or its ester, and the 2-oxochromen-3-carboxylic acid obtained is decarboxylated:

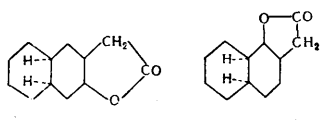


In the search for a more convenient method of synthesising coumarin, the preparation of the 3-carboxylic acid by interaction of salicylaldehyde and sodium cyanoacetate has been studied; sodium cyanoacetate is an intermediate in the production of malonic ester[250].

A method proposed[251] in 1958 for the conversion of 2-oxochromen-3-carboxylic acid into coumarin, based on the addition of bisulphite to the double bond of the pyran ring with simultaneous elimination of carbon dioxide, has been successfully extended to the ester. High yields of coumarin indicate that the method is suitable for industrial use[252].

Some problems in the preparation of coumarin by the interaction of salicylaldehyde and acetic anhydride[253,254] have been examined. Belov *et al.*[255] report an improvement in the synthesis of salicylaldehyde by the Reimer–Tiemann reaction.

In work on the relation between odour and structure in organic compounds[256,257], a lactone of the octalin series, with the proposed structure (LII) or (LIII), has been synthesised; an analogue (LIV), with a t-butyl group instead of one of the cylcohexane rings, has also been synthesised. Both lactones have an agreeable sandalwood odour, that of the first being the stronger.



(LII) (LIII) (LIV)

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THE CHEMISTRY OF THE ODOUR OF FOODSTUFFS

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I. INTRODUCTION

The last few years have seen the introduction and vigorous development of a new field of chemistry — the chemistry of the odour of foodstuffs. This review considers the main lines of investigation from 1956 to 1961 on the chemistry of the odour of meat, fish†, bread, milk and milk products, cocoa, and coffee.

At present the primary task of the chemistry of odour is to investigate the connection between odour and the physicochemical nature of the material, and on this basis to construct a theory to explain the mechanism of the interaction of substances with the olfactory organs. A theory of odour will enable a directed "synthesis" of the aroma of food products to be achieved and an objective odour analyser to be created; such an analyser will find wide application not only in the food and perfumery industries, but also in chemistry as an improved method for the analysis of volatile compounds. In medicine it may be used as a sensitive diagnostic apparatus for various diseases associated with the disturbance of metabolism.

Investigations of the chemistry of odour should also help in solving many of the most important problems of the food industry, in the first place retention of the original odour of commercial food products, avoidance of undesired flavours, shortening of ripening periods, and prevention of aging processes. Of particular significance for the food industry is the creation of aromatic mixtures to reproduce the odours of foodstuffs. In the future, synthetic compositions of food aromas will have particular value in connection with the production of artificial food. Solution of the above problems requires the combined efforts of chemists, physiologists, microbiologists, and food technologists.

The rapid development of the chemistry of odour has been held back by the absence of proper methods of analysis. Our olfactory organs are unsurpassed as analytical devices, and the best methods of analysis cannot as yet compete with them. A man can, for example, distinguish vanillin at a concentration of 10^{-14}. Additional difficulties in studying the odour of food products arise because the odour and the taste of food are extremely closely related, and can be separated only with difficulty, especially in the case of products having little taste and aroma, the latter being perceived only during actual consumption. Analysis of the odour of food products is also made difficult by the fact that odour is associated with the presence of minute quantities of a mixture of volatile substances: for example, 1 kg of cheese contains 1–2 mg of the material responsible for its aroma. Moreover, the aromatic mixture which provides the odour of food products is a multicomponent composition, containing sometimes up to 70 volatile substances. It is not surprising therefore, that the main advances in the chemistry of odour have been made in the last five years, and are principally associated with the use of various types of chromatography, particularly gas chromatography. Investigation of the odour of food products has required specific methods for the isolation and identification of the volatile substances responsible for the odour.

II. METHODS OF ISOLATION AND IDENTIFICATION

Methods of Isolation

Steam distillation in a current of nitrogen at 1–2 mmHg and 35–40° is generally used to separate the odoriferous principles from the mass of foodstuff [1-5]. The aromatic substances are sometimes distilled under a high vacuum (10^{-5}–10^{-6} mmHg) in a film evaporator over the same temperature range; the distillate is collected in a series of traps cooled to temperatures of -10° to -180°. [6-10] When these methods of concentration are used, there is the possibility of a change in the composition of the aromatic material when the foodstuff is heated.

The aromatic substances are sometimes separated by centrifuging [11] or by repeated extraction with solvents [12]; with the latter method, possible losses of readily volatile substances must be borne in mind, as well as the danger of contamination by trace impurities present in the solvent.

† Section VI has been written by S. D. Sokolov.

The oil carrying the aroma of the food product, obtained by this concentration, is then separated into the various classes of compound, and the individual components are identified.

Methods of Identification

The substances responsible for the aroma of foodstuffs can be identified by any physical or chemical method which can detect small amounts of a material in a complex mixture. The methods most widely employed in recent years are the various forms of chromatography. For example, the carbonyl compounds present in the odour of all foodstuffs can be separated by paper chromatography of their 2,4-dinitrophenylhydrazones[5,6,13-15], by thin-layer chromatography[16], or on columns of various adsorbents[17-19]. The carbonyl compounds are regenerated from the 2,4-dinitrophenylhydrazones by boiling with γ-oxovaleric or α-oxoglutaric acid[20,21].

Gas chromatography is the most frequently used for the analysis of components of odours, mainly because of its high sensitivity: modern chromatographs can determine 10^{-13} mole of a substance. Because of this high sensitivity, preliminary concentration of the odour can in some cases be omitted[22,23]. Moreover, the high resolving power of gas chromatographs (up to several 10^4 theoretical plates) and the use of stationary phases of varying selectivity enable the components of the odour to be analysed without preliminary separation into different chemical classes, and their proportions to be determined. Recently analysis by gas chromatography has often been combined with mass spectrometry and spectrographic methods of analysis[9,22-26]. The presence of a compound in a mixture is considered proved, even without isolation, if the same retention time, infrared spectrum, and mass spectrum are obtained as for the known compound itself.

The analysis of odours by gas chromatography requires a knowledge of the possibilities and limitations of the different types of detector which may be employed.

Recently Buttery and Teranishi[22] made a special study of the efficiency of the various types of detector in the analysis of the odours of foodstuffs without preliminary concentration, using for analysis the vapour taken from above the surface of the food product. They found that the sensitivity of thermal-conductivity detectors was much reduced by the presence of water vapour in the sample. Moisture does not lower the sensitivity of flame-ionisation detectors, but these have the disadvantage of insensitivity to hydrogen sulphide and low sensitivity to other sulphur compounds[8]. Moreover, the effectiveness of most standard chromatographs with flame-ionisation detectors is reduced because the products are identified only by their retention times, and combination with mass-spectrometric and spectroscopic methods of analysis is impossible because of combustion of the material in the detector.

According to Buttery and Teranishi, the best results in the analysis of anhydrous mixtures are given by argon ionisation detectors with ^{90}Sr as β source[27,28]; detectors with ^{147}Pm [29] or RaD as β source or with ^{226}Ra [30] as α source are only one-half to one-third as sensitive. Although the sensitivity of an argon β-ionisation detector is reduced in the presence of water vapour, it can be successfully employed for the analysis of sulphur compounds; it was so used in 1961 for the analysis, without preliminary concentration, of the sulphur-containing compounds in the odour of cabbage[9].

Clearly, the most promising device for the analysis of an odour would be a chromatograph of semipreparative type fitted with a means for temperature programming containing a β-ionisation detector through which only a part (about 5%) of the flow of gas is passed. Automatic temperature programming would considerably simplify the analysis, because the substances responsible for the aroma boil over a wide temperature range. Such a chromatograph could provide for simultaneous analysis of the components of the odour by mass-spectrometric and spectroscopic methods.

A more complete separation and identification of the compounds in aromatic mixtures by gas chromatography is generally carried out by using several columns with stationary phases of different polarity. Apiezon and silicone vacuum greases are used as non-polar phases, and polyglycols and their esters as polar phases.

Gas chromatography has provided rich new possibilities for the study of the chemical composition of food odours, but nevertheless the experience of recent years shows that the sensitivity of even the best chromatographs is still insufficient for the qualitative and quantitative determination of the composition of aromatic mixtures.

There is as yet not a single food product for which the composition of the materials responsible for its aroma has been fully determined. Further improvement in the analytical methods is required for the successful development of the chemistry of food odours.

III. THE ODOUR OF MILK AND MILK PRODUCTS

1. Milk, Cream, Butter

Flavours. The study of the aroma of milk and milk products has been stimulated primarily by the need to understand the reasons for the presence in them of tainted flavours, so that the latter may be avoided. There has been much study of the most frequently met taint in milk products, the "oxidised" flavour[4,31-37]. The "oxidised" flavour of milk, cream, and butter is due to autoxidation of the milk fat, the flavours at different stages of the oxidation being named separately. The first stages of oxidation are generally characterised by "cardboard", "oily", "drying oil", and "cucumber" flavours, and the later stages give rise to "mushroom", "tallowy", "fishy", and finally "metallic" flavours in the milk or milk product. These tastes appear particularly rapidly when the milk product is illuminated. The presence of copper‡ also greatly increases the rate of oxidation[38]. The mechanism of the catalysis of the oxidation of fats by metals of variable valency has been investigated in detail[40].

Investigations have shown that carbonyl compounds are the main causes of the oxidised flavour of milk and milk products. The reproduction of this flavour requires a whole complex of the saturated and unsaturated carbonyl compounds produced in the oxidation. The various shades of flavour are produced by an excess of one or more of the carbonyl compounds.

‡ The copper content of milk varies from 0 to 128 μg litre^{-1}.[39]

Day and Lillard[4,41] have compared the compositions of the carbonyl compounds in fresh and oxidised milk fat (Table 1). It is seen that the aroma of milk fat is produced by at least 27 carbonyl compounds — the C_1–C_{10} normal aldehydes, C_3–C_{11} α-unsaturated aldehydes, C_3–C_{15} methyl ketones, and hepta-2,4-dienal. The quantity of unsaturated carbonyl compounds increases with the degree of oxidation; for example, milk fat having a fishy taste, which appears at a later stage in the oxidation, contains more of the unsaturated aldehydes, especially hepta-2,4--dienal.

Table 2 gives the various flavours of oxidised milk fat arising because of the presence of an excess of one or more carbonyl compounds over the general level of carbonyl compounds present in the aroma of fresh milk fat.

El Negoumy *et al.*[40] synthesised the C_5–C_{10} alka-2,4--dienals, and determined the odour which they give to milk.

TABLE 1. Percentage content of carbonyl compounds in the odour of fresh and oxidised milk fat*.

Carbonyl compound	Fat with tallowy flavour	Fat with fishy flavour	Fresh fat	Carbonyl compound	Fat with tallowy flavour	Fat with fishy flavour	Fresh fat
C_1+C_2-al	32.47		0.7	C_{11}-one			0.13
C_3-al	5.04		0.07	C_{13}-one	4.01		
C_4-al	1.41			C_{15}-one			
C_5-al	9.96	4.0		C_3-enal			
C_6-al	9.23	25.0	0.14	C_4-enal	0.42		
C_7-al	18.80	20.0	0.16	C_5-enal	1.46	3.0	0.07
C_8-al	3.28	1.0		C_6-enal	0.38	4.0	
C_9-al	2.70	5.0	0.07	C_7-enal	1.91	3.0	
C_{10}-al	1.82	1.0	0.18	C_8-enal	0.66	2.0	
C_3-one				C_9-enal	4.18	5.0	0.06
C_5-one				C_{10}-enal	1.28		
C_7-one				C_{11}-enal			
C_9-one				C_7-2,4-dienal		8.0	

* The content of some of the compounds listed has not been determined.

TABLE 2. Substances producing various flavours in milk and milk products.

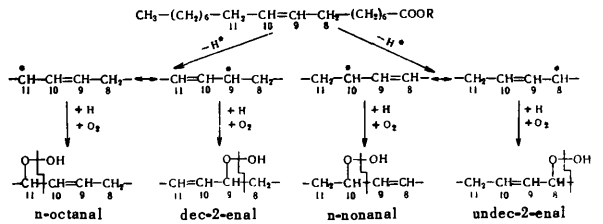
No.	Flavour*	Substances causing the flavour	Ref.
1	Cardboard and tallowy	n-octanol, oct-2-enal, n-nonanal, hepta--2,4-dienal, non-2-enal, undecanal**	34, 35, 40
2	Oily	n-pentanal, n-hexanal, n-heptanal, hex--2-enal, penta-2,4-dienal, deca-2,4--dienal	42–44
3	Drying oil	n-butanal, n-pentanal, pent-2-enal	45, 46
4	Mushroom	oct-1-en-3-one, heptan-2-ol	47
5	Cucumber	non-2-enal	48
6	Metallic	oct-1-en-3-one	47
7	Sunlight	methional	12, 49–52
8	Cereal	5-hydroxymethylfurfural, furfural, isobutanal, isopentanal, 5-methyl-furfural	53, 54
9	Acetone	acetone, acetoacetic acid, β-hydroxy-butyric acid	55, 56
10	Malty	isovaleraldehyde	37, 57–60
11	Coconut	δ-decanolactone, δ-dodecanolactone	12, 61–63
12	Bitter	monobutyrin, dibutyrin	64

* 1–6 are flavours arising by autoxidation of milk fat, milk, and milk products; 7–12 are flavours not associated with autoxidation of milk fat.

** Undecanal alone imparts a "grassy" odour to milk.

The C_7–C_{10} alkadienals produced an oily flavour, not immediately, but after a certain time, sometimes 5 min. A similar effect was observed by Patton[42], who produced an oily flavour in milk by adding 10^{-6} part of deca-2,4-dienal. The appearance of this flavour may be due to reaction of dienals with some constituents of the milk, since water does not acquire an oily flavour when C_7–C_{10} dienals are added to it. According to Hoffman[65] the oily flavour may depend also on the distribution of the dienal in the various phases of the milk. It is also possible that the stereochemical structure of the dienal has some significance. Synthetic dienals are in the *trans–trans* form, while the dienals isolated from milk fat contain also some *cis–trans* form. Recently Stark and Forss have shown[47] that the addition of 10^{-8} part of oct-1-en-3-one to milk produces a metallic flavour, confirmed by a tasting test. Addition of this ketone in amount close to the threshold of odour produces a mushroom flavour in milk and a flavour close to the cardboard flavour in skimmed milk. The threshold for oil and water was also shown to be 10^{-9} and 10^{-10} part of oct-1-en-3-one respectively.

It is now firmly established that unsaturated acids (oleic, linoleic, linolenic, etc.) present in milk fat may be the precursors of saturated and unsaturated carbonyl compounds. It has recently been confirmed experimentally that oxidation products of linoleate and linolenate impart an oxidised taste to milk[66]. The formation of carbonyl compounds by the oxidation of an oleate may be represented:



The oxidation of fats has been considered in terms of the chain theory in a recent monography by Emanuel' and Lyaskovskaya[67], which also considered the inhibition of the autoxidation of fats and gave a list of the antioxidants used in different countries for the preservation of fat-containing food products. The use of sodium gentisate (2,5-dihydroxybenzoate) has recently been proposed for preventing the oxidised flavour in milk and cream and increasing their storage life[68]. With the addition of 0.004% of sodium gentisate, cream and milk can be kept at -23° for six months, even if they contain copper. Table 2 shows the compounds responsible for the flavours not associated with autoxidation of milk fat.

Prolonged boiling of milk produces a "cereal" odour (the odour of "toasted cereal"). This odour is generally inherent in dried milk. Bassette and Keeney[53,54] investigated the odour of milk having a cereal flavour, identified a number of volatile carbonyl compounds, and determined the content of some of them (Table 3).

It is seen from Table 3 that, compared with fresh milk fat, fat-free dried milk contains additionally isobutyraldehyde, isovaleraldehyde, furfural, 5-methylfurfural, and 5-hydroxymethylfurfural, the last apparently having the most significance.

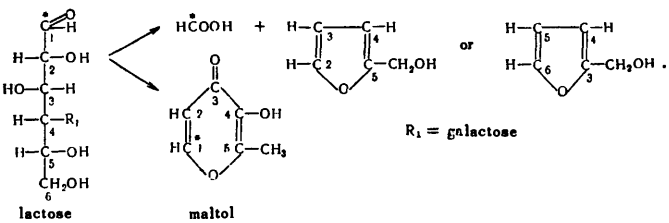
Keeney was able to reproduce the cereal odour by adding 5 micromoles of 5-hydroxymethylfurfural per litre of milk[54],

TABLE 3. Carbonyl compounds isolated from fat-free dry milk with "cereal" flavour.

Carbonyl compound	Content in milk, μg litre^{-1}	Carbonyl compound	Content in milk, μg litre^{-1}
Isobutyraldehyde	0.33	Formaldehyde	1.92
Isovaleraldehyde	0.17	Acetaldehyde	11.90
Hexanal	0.38	Acetone	7.20
Heptanal	0.23	Furfural	*cis*-2.38 *trans*-1.20
Octanal	0.17	Butanone	0.21
Nonanal	0.46	5-Methylfurfural	
Dodecanal	2.82	5-Hydroxymethylfurfural	

and he made the very likely suggestion that 5-hydroxymethylfurfural, furfural, and methylfurfural are formed by the Maillard reaction between lactose and the milk amino-acids.

Patton[69-72] was the first to obtain information on the part played by the Maillard reaction in the chemical reactions of the organic constituents of milk under the influence of heat. He showed that when milk is heated, [1-^{14}C]lactose produces, in the presence of milk proteins, labelled maltol [3-hydroxy-2-methylpyran-2-one] and formic acid and unlabelled furfuryl alcohol. Patton suggested the following process for the formation of these compounds:



Patton showed[49] that the "sunlight" flavour is due to the accumulation of methional [β-methylthiopropionaldehyde] in the milk. This is the flavour acquired by milk on exposure to sunlight. The methional is produced by oxidation of the methionine present in the milk casein:

$$CH_3S{-}CH_2{-}CH_2{-}CH(NH_2){-}COOH \xrightarrow{O} CH_3S{-}CH_2{-}CH_2{-}C(=O)H + NH_3 + CO_2.$$

The presence of riboflavin in the milk promotes the formation of methional. The addition of 5×10^{-8} part of methional to milk gives the typical sunlight odour.

An excess of compounds producing the "acetone" flavour in milk (see Table 2) is due to the activity of intestinal microorganisms (*Bact. cloacae*) and also to ketosis in the cow[53,54].

A "malty" flavour in milk and milk products is produced by isovaleraldehyde[37,57-60], which is assumed to be formed by the microbiological fermentation of leucine:

$$(CH_3)_2CH{-}CH_2{-}CH(NH_2){-}COOH \xrightarrow{O} (CH_3)_2CH{-}CH_2{-}C(=O)H + NH_3 + CO_2.$$

A common taint in milk and milk products is a bitter taste. An investigation into the causes of this taste showed that bitter fat contains 4–5 times as many free hydroxy-groups as does fresh fat. Ljunggren and Storgards consider that the bitter taste is imparted to milk and milk products by monobutyrin and dibutyrin, which they were able to isolate[64].

A "coconut oil" flavour is met with in milk, cream, and especially butter. Patton and his coworkers established[49-51] that it arises when the milk or milk product contains an excessive amount of δ-decanolactone or δ-dodecanolactone, the odour threshold of the former in milk being 10^{-6} part. Patton notes that unboiled fresh milk does not contain these lactones, which appear only when milk or cream is heated.

Patton also showed[12] that the bad odour of γ-irradiated milk is due to acetaldehyde, methanethiol, methyl sulphide, and methyl disulphide.

On the basis of the investigations reviewed, it may be considered established that the flavour of milk and milk products is most often due not to one, but to several compounds, the odour being greatly dependent on their concentration and on the properties of the medium to which they are added. Some confirmation of this is found in the interesting results obtained by Patton and Josephson[73] in their determination of the odour thresholds of certain volatile compounds present in the aroma of milk and milk products (Table 4).

It is seen, for example, that 0.05 mg of methional per litre gives skimmed milk a brothlike odour. As already indicated above, addition of this amount of methional to whole milk produces a sunlight flavour. Methional itself smells of raw pumpkin. Unfortunately, the absence of reliable objective evaluation of odour in many cases makes analysis of published data difficult.

Odours. The investigation of taints in the taste of milk and milk products has accumulated a large amount of information on the composition of the volatile substances which impart the aroma to fresh milk and milk products. The odoriferous components of milk and milk products include aldehydes, alkyl methyl ketones, acids, lactones, amines, and sulphur compounds. Currently there is vigorous activity on the quantitative determination of each component. Table 5 contains data on the qualitative composition of the aroma of milk and milk products, obtained by various workers in recent years.

It is seen that this aroma contains all the saturated straight-chain aldehydes, except butyraldehyde, from C_1 to C_{10}, and in addition isobutyraldehyde, isovaleraldehyde, hepta-2,4-dienal, pent-2-enal, non-2-enal, furfural, and benzaldehyde.

Unbranched methyl ketones with an odd number of carbon atoms, from acetone to pentadecanone, make up a substantial part of the aroma of milk and milk products, and there are present only two ketones — butanone and hexanone — with an even number of carbon atoms. The quantitative content of various aldehydes and ketones in milk fat[4] has already been given in Table 1.

TABLE 4. Odour threshold for some compounds in various media.

Compound	Medium	Threshold, mg litre^{-1}	Odour
Butyric acid	milk	25	rancid milk
Hexanoic acid	milk	14	rancid milk
Acetaldehyde	skim milk	1.3	burnt, malty
Acetone	ditto	500	chemical, medicinal
Butanone	»	50	fermented, sour milk
Methional	»	0.05	brothlike
Methyl disulphide	»	0.021	putrid, burnt
Dimethyl sulphide	water	0.012	malty, "cowy"
Methanethiol	water	0.002	boiled cabbage

TABLE 5. Compounds found in the aromas of milk and milk products.

Class of compound	Compound			Ref.
Aldehydes	formaldehyde acetaldehyde propionaldehyde valeraldehyde hexanal	octanal nonanal decanal* isobutyraldehyde isovaleraldehyde	pent-2-enal non-2-enal hepta-2,4-dienal furfural benzaldehyde	74–79
Alkan-2-ones	acetone butanone pentanone	hexanone nonanone undecanone	tridecanone pentadecanone	4, 78, 80–82
Acids	formic acetic propionic butyric hexanoic	octanoic decanoic lauric tridecanoic* myristic	pentadecanoic* palmitic margaric stearic	74, 83, 84
Amines	ammonia methylamine	ethylamine butylamine	diethylamine pyrrolidine*	85–87
Sulphur compounds	methanethiol methyl sulphide	methyl disulphide hydrogen sulphide	methional	12, 81, 88
Lactones	δ-decanolactone	δ-dodecanolactone		12, 89
Multifunctional compounds	biacetyl	acetoin		87, 90–96

* The presence of these compounds is not yet firmly established.

In 1962 Patton and his coworkers determined the amounts of various carbonyl compounds found in the aroma of heated cream and milk[79] (Table 6).

Patton has also shown[78] that the content of carbonyl compounds increases with the time of heating milk and cream; the heptanone content, for example, increased several hundredfold on heating.

The aroma of milk and milk products contains all the unbranched saturated acids from formic to myristic, with the exception of valeric, heptanoic, and nonanoic (Table 5). Formic, acetic, propionic, butyric, and hexanoic acids are present as such in milk. A litre of milk can contain up to 35 mg of butyric acid and 27.5 mg of hexanoic acid[84]. Acids containing an even number of carbon atoms from C_8 to C_{18} are found as the triglycerides, which are volatile in steam[74,83]. Aliphatic acids with an odd number of carbon atoms (C_5, C_7, C_9) have been found in oxidised milk fat[83].

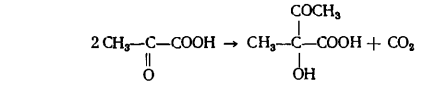
Other acids which affect the taste and possibly the aroma of milk and milk products include lactic and pyruvic acids[84,97,98], α-oxoglutaric, acetoacetic, oxaloacetic, and oxalosuccinic acids[98,99], and citric acid[100,101]. The content of free acids increases when milk and milk products are heated.

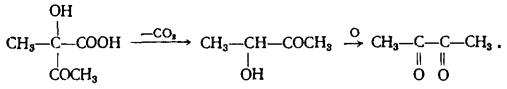
δ-Decanolactone and δ-dodecanolactone have been detected in pasteurised milk, and in cream and butter[12,89]. Lactones apparently make up a substantial part of the aroma of fresh butter, and the use of various δ- and ε-lactones for flavouring margarine has been patented in England, the U. S. A., Germany, and Australia[102–105].

Although present in minute amounts, sulphur compounds play a substantial part in forming the aroma of milk. In 1956 Patton and coworkers[106] isolated methyl sulphide from the volatile components of milk, and they later found methanethiol, methyl disulphide, methional, and hydrogen sulphide[12,81,88].

Recently ammonia, methylamine, ethylamine, and butylamine have been detected among the volatile components of milk and milk products[85–87]. Pyrrolidine may also be present, but this has not yet been definitely established[85].

Biacetyl is also a substantial component of the aroma of cream and fresh butter, being produced by the lactic acid bacterium *Betacoccus cremoris* from the pyruvic acid present. α-Acetyllactic acid is first produced, and on heating is decarboxylated and oxidised by atmospheric oxygen to biacetyl[87,90–92]:





The content of biacetyl in butter varies from 0.56 to 1.0 mg kg^{-1}.[93,95] It is often used for flavouring butter substitutes. Because of the experimental data on the mechanism of formation of biacetyl in butter, it has been proposed to add α-acetyllactic acid during the production of margarine[96]. A Japanese patent[107] for imparting an aroma to butter and margarine recommends the use of the mixture indicated in Table 7.

Until recently it was thought that, in addition to biacetyl, acetoin also plays an important part in the odour of butter and cream; in fact, acetoin purified by gas chromatography has no odour[108].

The aroma and taste of milk and especially of butter depend on the season; those of summer butter, for example, differ from those of winter butter, because of the different composition of the milk fat. Study of this composition is particularly important for the determination of possible precursors of the volatile compounds responsible for the odour.

Until recently it was thought that animal fats contain triglycerides only of straight-chain acids with an even number of carbon atoms, but it has since been established[109–116] that milk fat contains the triglycerides of C_4–C_{10} straight- and branched-chain, even and odd acids, with the exception of valeric acid.

TABLE 6. Content of some carbonyl compounds in the volatile components of milk fat, milk, and cream.

Compound	Content, mg $litre^{-1}$		Compound	Content, mg $litre^{-1}$	
	milk	cream		milk	cream
Formaldehyde	0.001–0.003	0.001–0.004	Pentanone	0.026–0.007	0.025–0.045
Acetaldehyde	0.016–0.013	0.001–0.004	Hexanone	0.007–0.011	0.017–0.018
Acetone	1.152–1.847	0.354–0.508	Heptanone	0.000–0.000	0.004–0.007
Butanone	0.077–0.079	0.154–0.177			

TABLE 7. Composition for imparting aroma to butter and margarine[7].

Mixture A, ml		Mixture B, ml		Mixture C, ml		Recommended for aroma, %	
Biacetyl	7	tetradecanal	6	ethyl acetate	9	mixture A	15
Isovaleric acid	3	lauric acid	6	ethyl lactate	9	mixture B	35
Acetaldehyde	2	vanillin	6	ethyl formate	9	mixture C	15
		butyl phthalate	18	ethyl butyrate	9	α-bromobutyric acid	35

Milk fat contains both conjugated and unconjugated unsaturated acids. McDowell[117] and Stadhouders and Mulder[118] have determined the contents of conjugated and unconjugated octadecadienoic and octadecatrienoic acids in winter and summer milk fat (Table 8).

It is interesting that the C_{18} acids contain a maximum of three double bonds. The infrared spectra of the C_{20} and C_{22} acids show them to include acids with four, five, and even six double bonds[119]; milk fat also contains a small quantity of branched-chain saturated acids[120-123].

The data so far obtained are sufficient to indicate the main pathways by which the volatile compounds present in the aromatic compositions responsible for the odour of milk, cream, and butter are produced. The chief precursors of the materials responsible for the aroma are apparently the milk fat and amino-acids present in milk. Particular importance attaches to reactions involving cleavage of the milk fat (primarily autoxidation) and to enzymic cleavage of the amino-acids. Moreover, a large part in the formation of the volatile components responsible for the odour of milk and milk products is played by reaction of the amino-acids with lactose (the Maillard reaction).

2. Cheese

The aroma of cheese is considerably different in chemical composition from that of other milk products; it contains a large number of esters and alcohols, and no unsaturated aldehydes. This is due to the technology of cheese production, which includes two most important steps — inoculation of the milk with cultures of bacteria such as *Streptococcus thermophilus*, *Lactobacillus bulgaricus*, *Propionibacterium shermanii*, *Streptococcus faecalis* *Lactobacillus lactis*, etc., and addition of rennin. The aroma and the taste of cheese are considerably affected by the microbiological and chemical composition of the milk, the types and activity of the cultures used, the amount of rennin added, the temperature and duration of ripening, the enzymes present in the cheese mass, and the enzymes which develop during its ripening.

Investigation of the aroma of cheese began with a study of the composition of the fatty acids, since butyric and propionic acids are often found in the odour of cheese. The early unsuccessful attempts to correlate the odour of cheese with the aliphatic acid content[124-128] were due to the use of insufficiently sensitive methods of analysis. In 1949 Peterson *et al.*[129], using their chromatographic method for aliphatic acids[130], studied the appearance and accumulation of acids during the ripening of Cheddar cheese, and found acetic, propionic, and butyric acids to accumulate during the first 30 days, after which hexanoic, octanoic, and decanoic acids appear. The content of C_6 and higher aliphatic acids in the cheese increases continuously as it ripens and ages. These workers suggested that the acetic acid is produced microbiologically from lactose, since the latter completely disappears from the cheese mass during the first few days of maturation. Other cheeses, such as Provolone, Rumanian, Swiss, and Blue, contain the same aliphatic acids as Cheddar, but a particular acid predominates in each type of cheese — *e.g.* acetic acid in Cheddar[131], butyric acid in Provolone and Romano cheese[132-135], and propionic acid in domestic Swiss cheese[136] (Table 9).

Russian cheeses have been studied by Chebotarev[137], who found Yaroslav cheese to contain most propionic acid, and Soviet cheese butyric.

In their study of the influence of various types of lipolytic enzyme preparations on the accumulation of free aliphatic acids in Italian cheeses (Provolone, Romano), Long and Harper showed[134,138] that the rate of formation and the concentration of butyric acid depend directly on the type of enzyme preparation (rennin) used for production of the cheese.

It can now be considered as established that, as the cheese ripens, the amount of the acid characteristic of that type of cheese increases, reaches a maximum in the mature cheese, and then decreases. The content of C_6 and higher aliphatic acids increases continuously with the time of storage of the cheese, irrespective of its type. Moreover, the suggestion made by Peterson and Johnson in 1949, that the aliphatic acids are produced by enzymatic cleavage of milk fat contained in the cheese, has also been confirmed. However, the aliphatic acids found do not reproduce the aroma of cheese, and Dacre has suggested[139] that in general fatty acids play no part in its production.

No direct relationship has been found between the quality of a cheese and its amino-acid content, but the number of free amino-acids in cheeses does not correspond to the composition of hydrolysed milk casein.[131,134,136-138,140-143] The amino-acid composition of ten types of USSR cheese has been studied by Chebotarev[137], who showed that such amino-acids as arginine, serine, methionine, and in some cheeses histidine are decomposed; ornithine and α- and γ-aminobutyric acids are produced. The accumulation of amino-acids during the ripening of Emmenthal cheese has been studied by Italian workers[144,145]. In 1956 Long and Harper suggested[138] that threonine, methionine, and histidine, which are present in small amounts in cheese,

TABLE 8. Content of conjugated and unconjugated acids in milk fat.

No. of C atoms in acid / No. of double bonds	Content in milk fat, %*	
18 : 2 conjugated	0.8–1.3;	0.58–2.81
18 : 2 unconjugated	0.2–0.7;	0.73–1.90
18 : 3 conjugated	0.03–0.04;	0.015–0.026
18 : 3 unconjugated	0.5–1;	0.35–0.96

* The first column gives McDowell's results, and the second Stadhouders and Mulder's; in each column the first figure is for winter milk fat, and the second for summer.

TABLE 9. Content of aliphatic acids in various types of cheese.

Cheese	Age of cheese	Acid content of cheese, mg g^{-1}			
		acetic	propionic	butyric	C_6 and higher
Swiss	3 months	2.6	4.4	1.2	2.4
	4 months	1.8	3.1	1.6	5.0
	11 months	3.0	5.0	1.1	24.2
Provolone	1 day	0.65	0.50	2.10	
	5 months	2.37	1.78	8.90	
	9 months	0.31	0.35	1.24	
Cheddar	mature, highest quality	23.5	1.6	0.7	11.0

play an important part in the metabolism of the bacteria, and that their conversions may be important in producing the odour of cheese. They showed that the amino-acid composition varies with the bacterial starter used, *i.e.* that the microbiological flora plays the main part in the accumulation of free amino-acids. For example, if *Lactobacillus lactis* is used in the production of Provolone cheese, the free amino-acid content is considerably greater than if *Lactobacillus bulgaricus* is used.

The accumulation of aliphatic acids and amino-acids in cheese is thus an indication of the enzymatic and bacteriological processes occurring during its production. In fact, a parallel study of the accumulation of fatty acids and amino-acids in Swiss cheese has shown[136] a clear relationship between the aroma and taste of cheese and its content of propionic acid and proline. Fig. 1 shows that, as the cheese ripens, the proline content rises from 0 to 4.5 mg × × g^{-1}, and then decreases as the cheese ages.

In cheeses of good taste and organoleptic evaluation the proline content is more than 2 mg g^{-1}, and the propionic acid content is about 4.5 mg g^{-1}. With smaller concentrations but about the same relative proportions of the two compounds (1 : 2), the odour is weak; when this proportion is disturbed, defective odours occur.

n-Butyric and glutamic acids play a definite part in the odour of Romano cheese[138], their contents in good-quality cheese being 3.0–7.1 and 4.8–6.3 mg g^{-1} respectively. Samples with less than these amounts had a poor aroma. For best-quality Provolone cheese the ratio of n-butyric to glutamic acid is about 1 : 2.

In 1960 Kristoffersen and Gould investigated the aroma of Cheddar cheese in relation to the amino-acid and aliphatic acid content[131], and concluded that the characteristic odour of the cheese is due to the simultaneous action of fat-splitting and protein-splitting agents. They followed the changes in the relative proportions of fatty acids to hydrogen sulphide (the latter being used to follow the rate of microbiological cleavage of the amino-acids) during the ripening of the cheese, and also in cheeses of various taste evaluations. The data in Table 10 show that the ratio of total aliphatic acids to hydrogen sulphide is characteristic of each type of odour. In cheese of normal odour this ratio is twice that in samples with a hydrogen sulphide odour, and half that in samples with a fatty acid odour. It is of interest that samples of the cheese with a sharp hydrogen sulphide odour contained less hydrogen sulphide than samples without this defect.

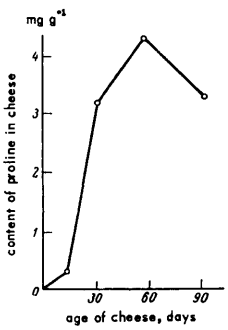


Fig.1. Variation of proline content with the time of ripening of Swiss cheese.

TABLE 10. Dependence of odour of Cheddar cheese on the relative proportions of aliphatic acids and hydrogen sulphide.

Odour	Aliphatic acids, mmoles g^{-1} / Hydrogen sulphide, mmoles $(100g)^{-1}$
Normal	17.6; 16.1; 13.1; 12.7; 11.7; 14.7;
Hydrogen sulphide	9.3; 8.7; 5.7; 5.1; 7.2;
Aliphatic acids	36.8; 30.0; 26.1; 22.8; 24.8; 27.8

The facts obtained in the simultaneous investigation of the rates of enzymatic splitting of fats and proteins during the making of different types of cheese thus show these rates to be an important factor in producing the odour of the cheese.

Alkyl methyl ketones, which are apparently present in all types of cheese, also play a significant role in the aroma of cheese[146-150]. In the investigation of the odour of Blue cheese in 1950, Patton isolated pentanone, heptanone, and nonanone[146]. Morgan and Anderson found the same ketones in Roquefort, Danish Blue, Gorgonzola, and Domestic Blue cheeses[147], and showed that all the samples of cheese having the typical odour contained acetone, pentan-2-one, heptan-2-one, and nonan-2-one; heptan-2--one or nonan-2-one was absent from samples having a weak aroma. Harvey and Walker[148] followed the contents of alkyl methyl ketones during the maturation of New Zealand Cheddar cheese (Fig. 2). The one-day old cheese contained acetaldehyde, acetone, butanone, and pentan-2-one. The acetone concentration fell to a minimum in two weeks, then rapidly increased to 4 mg g^{-1} in the 40-week cheese. The characteristic odour of Cheddar appeared after 8–12 weeks. The intensity of the odour increased with the content of pentan-2-one, heptan-2-one, and nonan-2-one. After 32 weeks undecanone appeared, and then rapidly increased in amount as the cheese ripened.

All the ketones, with the exception of butanone, may be produced as the result of fermentative splitting of the aliphatic acids of the milk fat, and this suggestion becomes very probable from the work of Foster[151], who showed that

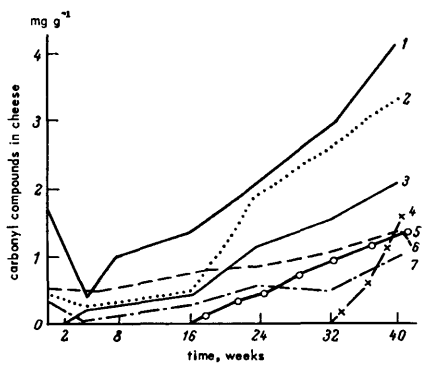


Fig.2. Change in concentration of carbonyl compounds during ripening of New Zealand Cheddar cheese:
1) acetone; 2) pentan-2-one; 3) heptan-2-one; 4) undecan-2-one; 5) nonan-2-one; 6) acetaldehyde; 7) butanone.

the enzymes produced by certain moulds, especially *Penicillium glaucum*, can convert all the individual acids from butyric to myristic into the corresponding methyl ketones:

$$R{-}CH_2{-}CH_2{-}COOH \xrightarrow{[O]} R{-}\underset{\underset{O}{\|}}{C}{-}CH_2COOH \rightarrow R{-}\underset{\underset{O}{\|}}{C}{-}CH_3 + CO_2 .$$

The mechanism by which butanone is produced has not yet been fully elucidated; Scarpellino and Kosikowski have recently suggested[26] its formation, together with butan-2-ol, from acetoin:

$$CH_3{-}\underset{\underset{O}{\|}}{C}{-}\underset{|}{CH}{-}CH_3 \xrightarrow{2H} CH_3{-}\underset{|}{\overset{|}{CH}}{-}\underset{|}{\overset{|}{CH}}{-}CH_3 \xrightarrow{-H_2O} CH_3{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}CH_3 \rightarrow$$

$$\xrightarrow{H} CH_3{-}CH_2{-}\underset{|}{\overset{|}{CH}}{-}CH_3 .$$

In 1962 McGugan and Howsam[8] employed a capillary column with a flame-ionisation detector for analysis of the volatile components of cheese, and detected 42 neutral compounds in the aroma, almost twice the number that had been known previously. Unfortunately, most of these were characterised only by their retention time. Table 11 lists all the volatile compounds found in cheese by McGugan and by other workers. It is seen that 64 compounds which give cheese its odour have been detected. Unfortunately, far fewer quantitative data exist.

TABLE 11. Volatile components in the aroma of cheese.

Compound	Ref.	Compound	Ref.
Aldehydes		*Esters*	
Formaldehyde	131, 152	Ethyl formate	8
Acetaldehyde	8, 147	Butyl formate	8
Propionaldehyde	8, 152	Methyl acetate	8
n-Butyraldehyde	8, 139	Ethyl acetate	8
Isobutyraldehyde	8	Isopropyl acetate	8
n-Valeraldehyde	8	Butyl acetate	8
Isovaleraldehyde	8, 152	Pentyl acetate	8
n-Heptanal	8	Isopentyl acetate	8
		Ethyl propionate	8
Ketones		Propyl propionate	8
Acetone	8, 24, 131, 147–149, 152	Isopropyl propionate	8
		Pentyl propionate	8
Butanone	8, 24, 148, 149, 152	Methyl butyrate	8
		Ethyl butyrate	8
Pentan-2-one	8, 146–149, 152	Butyl butyrate	8
		Methyl hexanoate	8
Pentan-3-one	8		
3-Methylbutanone	8	*Sulphur compounds*	
Heptan-2-one	8, 24, 146–149, 152, 153	Hydrogen sulphide	158–160
		Methyl sulphide	24
		Methional	152
Heptan-3-one	8		
Heptan-4-one	8	*Amines*	
Octan-2-one	8		
Nonan-2-one	146–149	Putrescine	161
Undecan-2-one	148–149	Tyramine	161
Tridecan-2-one	148	Tryptamine	161
		Histamine	161
Alcohols		Cadaverine	161
		Ammonia	160, 162
Methyl	8, 153		
Ethyl	8, 24, 139		
n-Propyl	8	*Other compounds*	
Isopropyl	8		
n-Butyl	8	Diacetyl	8, 24, 152, 153
Isobutyl	8		
s-Butyl	8	Pentane-2,3-dione	8
Isopentyl	8	Acetoin	24, 152
Acids			
Formic	154		
Acetic	155, 156		
Propionic	133, 156		
n-Butyric	155, 156		
Valeric	155		
Hexanoic	155		
Decanoic	155		

Walker and Harvey[149] determined the contents of certain carbonyl compounds in Cheddar cheese. Table 12 gives their results, together with the contents of some alcohols and ketones expressed as percentages of the total volatile compounds, as found by McGugan and Howsam[8].

In addition to simple ketones and alcohols, cheese contains considerable amounts of biacetyl and acetoin, but these compounds are apparently not specific components of the aroma of cheese, since their content decreases as the cheese ripens; moreover, as already stated, pure acetoin is odourless.

The volatile components of cheese include also ammonia and various amines. Ammonia was detected in cheese in 1959 by Moller-Madsen[162]. Kristoffersen and Gould[163] followed the changes in the concentrations of ammonia and hydrogen sulphide (Table 13). They comment that considerable variation in the ammonia content has no noticeable effect on the odour of cheese.

Silverman and Kosikowski investigated 23 samples of Cheddar cheese made from untreated and pasteurised milk, and detected putrescine, tyramine, tryptamine, histamine, and, in cheeses made from untreated milk, cadaverine also[161], the concentration of the amines in such cheeses being much greater than in cheeses from pasteurised milk. These workers consider that the amines which they found are produced by degradation of amino-acids by a specific decarboxylase arising as the result of bacterial activity; they suggest the following reactions for the formation of the amines

tyrosine → tyramine + CO_2,
lysine → cadaverine + CO_2,
arginine → urea, ornithine, putrescine + CO_2,

Sulphur-containing compounds form a substantial part of the aroma of cheese (Table 11); removal of these, as with alkyl methyl ketones, leads to loss of the characteristic odour of the cheese. Sulphur compounds are apparently produced by fermentative degradation of amino-acids:

TABLE 12. Content of volatile compounds in Cheddar cheese.

Compound	Content, mg kg^{-1}	Total volatile compounds, %	Compound	Content, mg kg^{-1}	Total volatile compounds, %
Acetaldehyde	2.65		Undecan-2-one	0.83	
Acetone		2.4–5.1	Tridecan-2-one	trace	
Butanone	0.80		Methyl acetate	0.86	
Pentan-2-one	2.47	5.7	n-Propyl alcohol		7
Heptan-2-one	6.6		Isopropyl alcohol		7.6–10.4
Nonan-2-one	1.7		s-Butyl alcohol		

TABLE 13. Change in concentration of ammonia and hydrogen sulphide during ripening of Cheddar cheese.

Compound	Milk used	Time of storage of cheese, months					
		0.5	1.5	3	6	9	12
NH_3	plain	7.9*	10.9	27.0	30.3	40.6	49.0
	pasteurised	8.8	8.8	22.8	28.6	35.1	44.9
H_2S	plain	2.3	3.7	2.4	3.2	2.4	2.3
	pasteurised	1.2	2.0	1.5	1.8	1.6	1.6

* Concentrations are given in micromoles per gramme of cheese for ammonia, and micromoles per 100 g of cheese for hydrogen sulphide.

thus Kristoffersen and Nelson[158] isolated from high-quality cheese strains of *Lactobacillus casei*, which can degrade cysteine with evolution of hydrogen sulphide.

Several workers have remarked that the taste qualities of cheese are affected by hydroxy-acids and di- and tri--carboxylic keto-acids present in cheese and cheese sweat. Chebotarev detected lactic, succinic, fumaric, oxalic, and glycollic acids in Soviet cheeses, gluconic acid in Latvian and Dorogobuzh cheeses, and citric acid in grated green cheese[137].

Kristoffersen and Gould[163] found α-oxoglutaric, α-acetyllactic, oxaloacetic, glyoxylic, γ-methyl-α-oxovaleric, and citric acids in Cheddar cheese.

In 1957 the Finns Kreula and Virtanen showed[164] that lactic and propionic acid bacteria produce the same α-keto--acids as are found in Emmenthal cheese and its sweat; they isolated glyoxylic, pyruvic, hydroxypyruvic, oxaloacetic, α-oxoglutaric, β-methyl-α-oxobutyric, and γ-methyl-α-oxovaleric acids. These results suggest that keto-acids are produced in cheese by the action of lactic acid bacteria.

Many attempts have been made to formulate artificial mixtures which reproduce the odour of cheese. Thus Dacre[139] tried, in various proportions and concentrations, pure and in solution, all normal alcohols and iso-alcohols up to isopentyl inclusive, all normal aldehydes and iso--aldehydes up to isovaleraldehyde inclusive, all methyl ketones up to methyl pentyl ketone inclusive, and all symmetrical ketones up to di-n-propyl ketone; ethyl formate, acetate, propionate, butyrate, hexanoate, pyruvate, and lactate; and methylglyoxal and butane-2,3-diol. In no case did he obtain a typical cheese odour.

In 1957 Keeney and Day reported[165] the approximate reproduction of cheese aroma by carrying out the Maillard reaction with isatin and an amino-acid mixture of similar composition to casein hydrolysate.

In 1961 Walker[166] accelerated the formation of the cheese aroma in a ripening cheese mass by adding a mixture of certain alkyl methyl ketones, free aliphatic acids, and thioacetamide as a source of hydrogen sulphide; Table 14 gives his suggested mixture. This was added to 20 g of melted butter and mixed with 4 kg of the cheese curd; after 3 weeks the cheese mass had the odour of 3-month Cheddar cheese.

Much is now known about the qualitative and in part the quantitative composition of the aroma of milk, cream, butter, and cheese, but the odour of none of these has yet been created artificially, and in no case can even the qualitative picture of the aroma be considered as complete. It is possible that a more thorough investigation employing improved methods of analysis will increase the number of components known to be responsible for the aroma of milk products. It is also possible that the quantitative proportions of already known components will prove to play the basic role in the aroma of milk and milk products. At present particular attention is being paid to the quantitative determination of each component of the aroma.

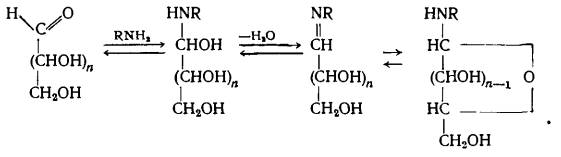
TABLE 14. Composition added to cheese curds to obtain the odour of three-month cheese in three-week-old cheese mass.

Mixture A, g		Mixture B, g		Composition recommended for 4 kg of cheese mass	
methyl ketone		acid			
Acetone	4	acetic	10	mixture A	0.3 ml
Butanone	1	n-butyric	5	mixture B	1 ml
Pentan-2-one	3	n-hexanoic	12	thioacetamide	0.1 g
Heptan-2-one	2	octanoic	14		
Nonan-2-one	1.5				
Undecan-2-one	1.5				
Tridecan-2-one	0.5				

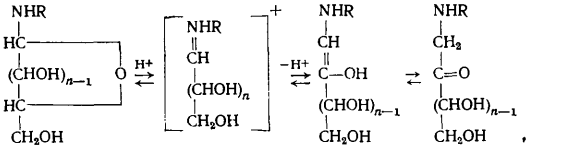
A reaction having great importance in the production of the aroma of nearly all food products is the Maillard reaction, especially where the aroma is produced by heating the foodstuff, for example in bread and meat.

The Maillard reaction. This has been the subject of several long reviews[167-169], and we shall therefore consider here only the suggested mechanism, and the attempts which have been made to obtain food odours by utilising this reaction.

The Maillard reaction is the reaction between an amino-group in an amino-acid, a peptide, or a protein and a glycosidic hydroxy-group in a sugar. The mechanism as a whole is very complex, and is not entirely clear: only the initial stages can as yet be considered proved. The first step is formation of an *N*-substituted glycosylamine



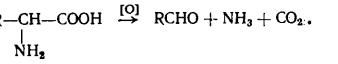
This then rearranges to produce a substituted 1-amino-1--deoxy-2-ketose (the Amadori rearrangement):



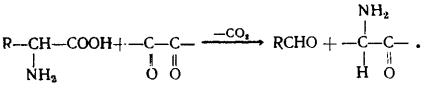
which then undergoes a series of reactions whose mechanism is not fully clear.

Products of the Maillard reaction include aliphatic aldehydes, furfural and certain furfural derivatives, formaldehyde, biacetyl, methylglyoxal, acetoin, and acetone.

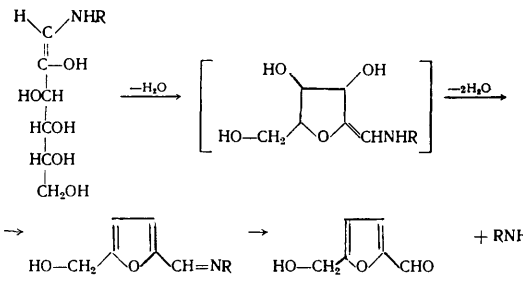
The aliphatic aldehydes are produced in the Maillard reaction by oxidative degradation of amino-acids, known as the Strecker reaction, which can be represented



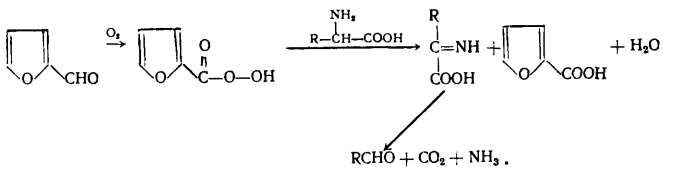
The resulting aldehyde contains one carbon atom less than the initial amino-acid. The Strecker degradation can occur by reaction of amino-acids either with the Amadori rearrangement product or with dicarbonyl compounds present in the reaction mixture



Furfural and its derivatives are produced by dehydration of the Amadori rearrangement product



According to this mechanism, furfural is produced from pentoses, hydroxymethylfurfural from hexoses, and methylfurfural from methylpentoses. Rothe and Thomas consider[170] that furfural and its derivatives can also participate in the Strecker degradation:



Other reactions of the Amadori rearrangement product have not yet been fully investigated.

The end-products of the Maillard reaction are the dark nitrogen-containing polymerisation and polycondensation products known as melanoidines; these play an important part in the darkening of food products, particularly when they are heated.

The Maillard reaction is catalysed by traces of moisture, is unaffected by atmospheric oxygen, and proceeds over a wide pH range, with an optimum in neutral or weakly alkaline media (pH 7–9). The rate of the reaction at 60° is 20 times that at 37°, but even at 37°, it is important to note, the reaction goes at an appreciable rate[167,171]. This suggests that the Maillard reaction may be involved, even at room temperature, in the formation of the substances responsible for the odour of food products.

There have been several hundred papers on the Maillard reaction, but information on the odour produced by the reaction in each particular case is very scanty.

In 1960 Herz and Shallenberger[172] investigated the aroma produced when various amino-acids are heated with glucose at 100° and 180° for 1 h; their results are given in columns 2 and 3 of Table 15. There is no definite relationship between the odour and the reaction temperature; for instance, with leucine and threonine the odour is pleasant at 100° but unpleasant at 180°, while the reverse is true with proline. With histidine an odour appears only at 180°. These workers showed that, irrespective of the temperature, glycine, α- and β-alanine, and glutamic acid produce only the odour of burnt sugar on reaction with glucose; tryptophan, tyrosine, arginine, and α-aminobutyric acid produce the burnt sugar odour only at 180°.

Keeney and Day[165] obtained various odours by heating a number of amino-acids with isatin at 100° in dilute hydrochloric acid for 15 min. No odours were produced by glycine, tryptophan, arginine, histidine, lysine, or aspartic acid (Table 15, column 1).

TABLE 15. Odours produced from amino-acids by the Maillard reaction.

Amino-acid	Odour, under the reaction conditions				
	100°, 15 min	100°, 1 h	180°, 1 h	95°, 1 h	
Glycine	none	burnt sugar	burnt sugar		
Alanine	malty	burnt sugar	burnt sugar		
Valine	apple	rye bread	penetrating, chocolate		
Leucine	malty	sweet, chocolate	burnt cheese*	rye bread	
Isoleucine	malty, apple	musty	burnt cheese*		
Proline	mushroom	burnt protein	pleasant, bakery		
Hydroxy-proline	none	none	none		
Phenylalanine	violets	violets	violets, lilac		
Tyrosine	none	none	burnt sugar		
Tryptophan	none	none	burnt sugar		
Cystine	hydrogen sulphide				
Methionine	cheesy–brothy	potato	potato		
Serine	none	none	none		maple syrup
Threonine	none	chocolate	burnt		maple syrup
Aspartic acid	none	rock candy	burnt sugar		almond
Glutamic acid		burnt sugar	burnt sugar		almond
Arginine	none	popcorn	burnt sugar		
Lysine hydro-chloride	none	none	breadlike		
Histidine	none	none	corn-bread		
α-Aminobutyric acid		none	burnt sugar		maple syrup
α-Amino-α--methyl-propionic acid					maple syrup
Asparagine		none	none		
Glutamine		chocolate	butterscotch		
Ref.	165	172	172	173	171

* Taken from Ref. 172, Russian text has "burnt sugar" (Ed. of Translation).

Comparison of the results given in Table 15 shows that the same amino-acid can produce different odours in the Maillard reaction, probably because of the different reaction conditions. The considerable subjectivity in the assessment of odour must also be taken into account.

Unfortunately, there are no data on the Maillard reaction with different amino-acids under comparable conditions. The effect of the sugar on the specificity of the resulting odour has been much investigated. On the basis of their results, Kretovich and Tokareva concluded that the nature of the sugar does not affect the type of odour[173]; thus leucine reacts with xylose, glucose, and fructose to give the same odour of rye bread. However, the sugar does influence the rate of the Maillard reaction. Pentoses, especially xylose, react the most readily; with hexoses the rate is somewhat lower. The specificity of the odour is determined by the amino-acid used.

There is no doubt that the Maillard reaction requires more detailed investigation from the point of view of the "synthesis" of food odours. Such investigation might in many cases explain the occurrence of odour in food products.

IV. THE ODOUR OF BREAD

About 75 volatile compounds have been found in the aroma of bread, of which more than 60 have been identified; these are mainly carbonyl compounds, lower aliphatic acids, alcohols, esters, and some sulphur compounds. The components of the odour are produced during the making of the bread, which comprises three stages — (1) fermentation in the leaven, (2) biochemical processes

in the dough, and (3) the baking of the bread. These processes make different contributions to the final aroma of the bread. Table 16 shows the qualitative composition of the odoriferous components of the leaven, the dough, and the bread. Ketones, certain esters and alcohols are produced during the fermentation in bread ferments obtained from bread yeasts and sugar with addition of some mineral salts; however, the quantity of aliphatic aldehydes, except for acetaldehyde, is considerably smaller in the ferments than in the baked bread. At this stage of bread production lactic, succinic, malic, tartaric, and citric acids are also formed, and these play a much more important part in producing the flavour; however, their esters contribute to the aroma of bread[174].

Biochemical processes in the dough lead to the formation of the aliphatic acids from propionic to decanoic. Bacterial action in the dough also produces certain aldehydes, and the content of keto- and hydroxy-acids increases.

Kohn *et al.* [195] have studied the content of carbonyl compounds in normal and low-bacteria dough, and have established that the normal microflora of dough has no marked influence on the bread aroma. However, it has been reported that the aroma of bread is considerably improved when cultures of certain bacteria are added to the leaven or the dough[188,195,199-201]. Thus Tokareva and Kretovich have shown that enzyme preparations from the moulds *Aspergillus oryzae* and *Aspergillus awamori* reduce the fermentation time in the leaven by 39–43%, increase the content of hexoses and pentoses in the bread, and improve its taste and aroma[199].

The ferments and dough contain substances which are not produced by the Maillard reaction, mainly acids, alcohols, and esters; the content of these decreases on baking. Wiseblatt[193] studied the concentration of volatile organic acids in the dough, the bread, and the oven gases (Table 17).

Baking is the most important stage in formation of aroma, since it is here that the characteristic odour of bread is produced. The main reaction in the formation of odoriferous substances during baking is that between amino-acids and sugars (the Maillard reaction), which leads to the production of a large quantity of these substances, including furfural, hydroxymethylfurfural, and aliphatic aldehydes[170,181,182]; they are mainly formed in the crust (the hottest region), and penetrate into the soft inner part by diffusion. It is the final reaction products, the melanoidines, which give bread-crust its dark colour[174,202]. The importance of the Maillard reaction in forming the aroma of bread is shown by a number of phenomena. Thus, bread baked from overfermented dough, in which all the sugar has been used up in the fermentation, has no aroma and a pale crust. If some sugar is added to such dough before baking, the resulting bread has the normal aroma and a crust of good colour. Comparative analysis of the oven gases from the baking of overfermented and normal dough shows that in the former case almost no furfural or methylglyoxal and very little aliphatic aldehydes are produced[174,181].

Rothe and Thomas[170] studied the variation of the content of furfural and other aldehydes with duration of the period of baking of normal bread (Table 18).

TABLE 16. Compounds involved in producing the aroma of bread.

Compound	Source*	Ref.	Compound	Source*	Ref.
Aldehydes			*Acids*		
Formaldehyde	F, B	17, 175, 176	Formic	F, B	190
Acetaldehyde	F, D, B, G	17, 174–180	Acetic	F, B, G	174, 175, 178, 190–191
Propionaldehyde	F, B	176	Propionic	F, B	190–192
n-Butyraldehyde	F, D, B	176, 177	n-Butyric	F, D, B	190–193
Isobutyraldehyde	F, B	17, 181, 176	Isobutyric	F, D, B	190, 192
n-Valeraldehyde	F, B, G	17, 176	n-Valeric	F, D, B	190–192
Isovaleraldehyde	F, D, B, G	17, 176, 177	Isovaleric	F, D, B	190, 192, 193
α-Methylbutyraldehyde	F, B	17, 176, 181	Hexanoic	F, D	190, 192, 193
n-Hexanal	F, D, B	17, 176, 177	γ-Methylvaleric	F	190, 192
2-Ethylhexanal	B	180	Crotonic	F	190
Crotonaldehyde	B	180	Heptanoic	F	190
Furfural	B, G	17, 170, 174, 175, 180–185	Octanoic	F	190
Hydroxymethylfurfural	B	186, 187	Nonanoic	F	190
Benzaldehyde	D	177	Decanoic	F	190
p-Hydroxybenzaldehyde	B	188	Lauric	F	190
Phenylacetaldehyde	B	181	Myristic	F	190
Cinnamaldehyde	B	188	Palmitic	F	190
Vanillin	B	188	Lactic	F, D, B	189, 194
Syringaldehyde	B	188	Succinic	F, D, B	194
Alcohols			Malic	F, D, B	194
Ethyl	F, D, B, G	176, 179, 180, 182	Tartaric	F, D, B	194
n-Propyl	F	175, 177, 181	Citric	F, D, B	194
2-Methylbutyl	B	17	Pyruvic	F, B	185, 195
n-Hexyl	B	17	γ-Oxovaleric	B	185
Phenethyl	F	179	*Sulphur compounds*		
Ketones			Hydrogen sulphide	B	175
Acetone	F, D, B	17, 176, 177, 179, 180	Methanethiol	B	175, 196, 197
Butanone	F, B	17, 176	Methional	B	181
Hexan-2-one	D, B	177, 180	*Other compounds*		
Heptan-3-one	B	180	Ammonia	B	192
Esters			Biacetyl	F, B	179, 180, 185
Ethyl acetate	F	189	Acetoin	F, B	179, 198
Ethyl lactate	F	179, 189	Butane-2,3-diol	F	179, 197
Ethyl γ-oxovalerate	B	180, 185	Methylglyoxal	D, B, G	174, 177, 180, 181
Ethyl pyruvate	B	17, 180, 185	γ-Butyrolactone	F	179
			3-Hydroxypropyl acetate	F	179

* F = ferment (leaven); D = dough; B = bread; G = oven gases.

TABLE 17. Volatile organic acids (mg kg^{-1} of flour) in bread, dough, and oven gases.

Acid	Dough	Bread	Oven gases
Acetic	198	150	15
n-Butyric	23.1	10.6	0
Isovaleric	13.1	6.1	0
Hexanoic	6.2	0	0

TABLE 18. Variation of content of furfural and other aldehydes in bread with time of baking.

Bread	Time of baking, min	Furfurol, mg %	Other aldehydes, mg %
White	40	0.25	0.15
White	90	0.3	0.3
Black	50	0.9	0.3
Black	90	1.05	0.7
Pumpernickel	1000	2.2	4.9

Confirmation of the decisive role of the Maillard reaction in the formation of the aroma of bread is the appearance of this aroma in model experiments conducted with valine, leucine, proline, and lysine (Table 15).

Rothe and Thomas consider[170] that six amino-acids of the grain — leucine, alanine, valine, isoleucine, phenylalanine, and methionine — are of particular importance in producing the aroma of bread at the baking stage, these being precursors of the aldehydes isovaleraldehyde, acetaldehyde, isobutyraldehyde, phenylacetaldehyde, and methional. Together with furfural and hydroxymethylfurfural, these aldehydes are the main components of the aroma of bread. Reaction of the carbonyl group of the aldehydes with dimedone greatly reduces the aroma of the bread[181,182].

Kretovich and Tokareva[187] have shown the aroma of bread to depend on the hydroxymethylfurfural content. Some part in producing the aroma of bread may be played by such aromatic aldehydes as vanillin, cinnamaldehyde, and syringaldehyde, found by Tokareva by paper chromatography[188]. The presence of these aldehydes requires confirmation by other methods of analysis, since they are not found in the odours of other food products.

Sulphur compounds are assumed to be important in producing the aroma of bread. Rothe ascribes particular importance to methional[181], and Rotsch and Dörner to methanethiol and hydrogen sulphide[175,196], all of which have been found among the volatile compounds responsible for the odour of bread.

Volatile acids do not apparently play a large part, since neutralising them has no marked effect on the aroma of bread[182]. Apparently biacetyl and acetoin, which had previously been regarded as the main ingredients of the aroma of bread[198], also play no important part, since no definite relationship has been found between their concentration and the aroma of bread[181,182,203]. Similarly no correlation has been established between the concentration of esters and the aroma of bread[181].

It is important to note that the odoriferous volatile components of bread readily undergo chemical changes, which on the one hand hinder study of the actual initial aroma, and on the other lead to a worsening of the aroma of bread on storage. Apparently the change in the odour of bread as it stales is not due to drying out or to a change in the structure of the bread, but to atmospheric oxidation of the volatile aldehydes[174]. When moist air is blown over bread crumb for 4 h, the bread remains soft but takes on the odour of stale bread. On standing, the condensate from the oven gases, initially containing the volatile components of fresh bread, also develops the odour of stale bread.

Various additives have been suggested for improving the aroma of bread. The national Russian odour-improver for bread is red rye malt obtained from germinated rye seed. The chemical composition of the aromatic substances of malt has been investigated by Kretovich *et al.*[204], who suggested that the furfural, hydroxymethylfurfural, and aliphatic aldehydes found in malt are products of the Maillard reaction taking place in the germinating rye seeds during production of the malt.

Hodge and his coworkers[205,206] proposed to improve the aroma of bread by adding to the dough maltol (3-hydroxy-2-methylpyran-4-one), isomaltol (structure unknown), and galactosylisomaltol, which have been isolated from bread and are intermediates in the Maillard reaction. These decompose during baking to produce substances which improve the aroma of the bread.

The formation of odoriferous compounds when sugar and milk are fermented with yeast has been utilised to prepare the dry odour-improving additive Vico-400, which is widely recommended for the production of aromatic bread[207].

In an attempt to reproduce artificially the aroma of bread, Wiseblatt[178] found the best aroma to be given by a mixture of the composition

Ethanol	4 g
Acetaldehyde	10 mg
Acetic acid	40 mg
Furfural	20 mg
Acetoin	6 mg.

Addition of this mixture to 180 ml of water gave an odour which was pleasant, but not quite like the aroma of bread.

It is thus seen that it has not yet proved possible to reproduce the aroma of bread chemically.

V. THE ODOUR OF COCOA AND COFFEE

The aroma of coffee and cocoa is formed in the fermentation and roasting of the coffee and cocoa beans; both these processes are extremely important for the production of coffee and cocoa of good taste properties. The significance of the fermentation in cocoa production has been much studied[208-211], the microorganisms involved including moulds (*Aspergillus*, *Mucor*, *Penicillium*, *Rhizopus*, etc.), yeasts (*Saccharomyces cerevisiae*, *Candida krusei*, *Kloeckera apiculata*, *Hansenula anomala*, etc.) and lactic acid and acetic acid bacteria[208]. The enzymes produced by the microorganisms decompose the polyphenols and proteins[212] contained in the cocoa beans. Unfermented cocoa beans do not give a chocolate aroma when roasted, but a strong aroma of ordinary roasted beans; they do not have a chocolate colour. The chemical reactions of the polyphenols during the fermentation were investigated by Forsyth[211,213-216], who isolated nine polyphenols from fermented cocoa beans. The polyphenol content was 7.8%, the main one being (-)-epicatechin[214]. Decomposition of the polyphenols when the cocoa beans are roasted evidently plays an important part in formation of the aroma of cocoa, since, when the polyphenols and organic acids are precipitated from alcohol extracts of the cocoa with lead acetate, no chocolate odour is produced on roasting. Amino-acids are also apparently important precursors of the cocoa aroma. Aspartic and glutamic acids, alanine, cysteine, leucine, serine, threonine, methionine, and arginine have been found in cocoa beans[217], and during roasting these are oxidised, deaminated, and decarboxylated: *i.e.* they undergo the Strecker degradation to form aldehydes[218].

The volatile substances in the aroma of cocoa were first investigated in 1912 by Bainbridge and Davies[219]; from 2000 kg of roasted cocoa beans they separated 24 ml of an aromatic oil, 50% of which was α-linalool; 10% of the mixture comprised esters of lower aliphatic acids.

Schmalfuss and coworkers[220,221] were the first to isolate from roast cocoa biacetyl and acetoin, which they considered to be important in the formation of the chocolate aroma, but in 1936 Fincke showed[222] that addition of biacetyl to cocoa powder does not improve its aroma.

Mohr in 1958[223] was the first to investigate the chocolate aroma by gas chromatography, and found 23 compounds.

In 1961 Dutch workers identified alcohols, aldehydes, and esters in the aroma of cocoa[224]; their findings are shown in Table 19, which also gives the amines found by Weurman and de Rooij in cocoa powder[85].

In 1962 Bailey *et al.*[218] used a high sensitivity chromatograph with a β-ionisation detector to study the aroma of six types of roasted cocoa beans — Accra, Arriba, Bahia, Trinidad, Winey, and Sanchez. The substances isolated were additionally investigated with a mass spectrometer.

The aroma compositions of the different types of roasted and raw cocoa beans were very similar, and apparently differed only in the content of certain of the components, mainly aldehydes. Thus the n-butyraldehyde content was greatest in the Bahia and Arriba types. Isovaleraldehyde, isobutyraldehyde, propionaldehyde, and acetaldehyde were present in greatest amount in all the types of cocoa bean. The accumulation of these aldehydes during the roasting of the cocoa was also studied by Bailey *et al.* (Fig. 3); the contents of all four aldehydes increase, especially that of isovaleraldehyde and isobutyraldehyde. These aldehydes are present to a negligible extent in the raw beans. The isovaleraldehyde is thought to be formed by decomposition of leucine. Sixteen compounds were found in the volatile fraction of roasted Bahia beans by the chromatographic and mass-spectrometric analysis (Table 20).

TABLE 19. Volatile compounds in the aroma of cocoa.

Class	Compound	
Alcohols	methyl ethyl propyl isopropyl isobutyl	isopentyl furfuryl linalool geraniol
Esters	ethyl acetate isopropyl acetate n-propyl acetate isobutyl acetate n-pentyl acetate	ethyl propionate pentyl propionate pentyl butyrate linalyl acetate
Carbonyl compounds	acetaldehyde α-citronellal	biacetyl 6-methylhept-5-en-2-one
Amines	methylamine isobutylamine dimethylamine	ethylamine isopentylamine

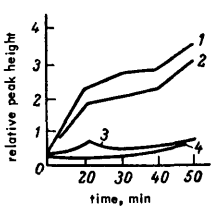


Fig. 3. Accumulation of aldehydes during the roasting of cocoa beans at 148.8°:
1) isovaleraldehyde;
2) isobutyraldehyde;
3) propionaldehyde;
4) acetaldehyde.

TABLE 20. Mass-spectrometric analysis of the aroma of roasted Bahia cocoa beans.

Compound	Content, mole %	Compound	Content, mole %
Isovaleraldehyde	42.0	Methyl sulphide	0.3
Isobutyraldehyde	15.4	Methyl disulphide	0.2
Propionaldehyde	13.0	Ethanol	0.2
Methanol	9.1	Furan	0.2
Acetaldehyde	7.0	Toluene	0.1
Methyl acetate	6.3	Benzene	0.1
n-Butyraldehyde	3.0	Methylfuran	trace
Biacetyl	2.8	Acetone	trace

The number of volatile components in the aroma of liquid cocoa is much less than in the powder; Bailey and his coworkers obtained only 8 peaks in the chromatogram of the aroma of liquid cocoa, of which only 5 were identified — acetaldehyde, methyl acetate, propionaldehyde, isobutyraldehyde, and isovaleraldehyde. These compounds cannot be wholly responsible for the aroma of cocoa.

As with cocoa, the aroma of coffee is formed during the fermentation and, especially, during the roasting. Again as with cocoa, the precursors of the aroma of coffee are apparently polyphenols and amino-acids. The first gas-chromatographic investigation of the aroma of coffee was made by Rhoades in 1958.[225] The volatile components were steam-distilled from roast coffee in a current of helium and analysed on a Perkin–Elmer chromatograph. The chromatogram showed 16 peaks, of which 7 were identified. These results, together with data on the qualitative composition of the aroma of coffee obtained by other workers, are given in Table 21.

In 1960 Zlatkis and Sivetz[226] investigated quantitatively coffee aroma essence, obtained from the condensed volatiles during roasting of the coffee, and the distillate obtained by vacuum distillation of roast coffee with steam.

TABLE 21. Volatile compounds found in coffee aroma.

Compound	Ref.	Compound	Ref.	Compound	Ref.
Aldehydes		*Esters*		*Nitrogen compounds*	
Acetaldehyde	56, 225	Ethyl formate	226	Ammonia	56
Propionaldehyde	225	Methyl formate	226, 227	Methylamine	56
Butyraldehyde	226, 227	Methyl acetate	226	Trimethylamine	56
Isobutyraldehyde	226, 227	Furfuryl formate	56	Pyridine	56, 228
Valeraldehyde	227	Furfuryl acetate	56	Pyrrole	56
α-Methylbutyraldehyde	56			*N*-Methylpyrrole	56
Furfural	56, 226, 228	*Acids*		Pyrazine	56
		Formic	56, 226		
		Acetic	56, 226	*Other compounds*	
Ketones		Propionic	56, 226		
		n-Butyric	56	Acetoin	56, 228
Acetone	56, 225, 226, 227	n-Valeric	56	3-Hydroxypentane-2,4-dione	228
		Isovaleric	56		
Butanone	225, 227	α-Methylbutyric	56		
Pentan-3-one	56	Hexanoic	56	2,3-Dihydroxyacetophenone	56
Biacetyl	225, 227	Octanoic	56		
Pentane-2,3-dione	56, 227			Isoprene	227
		Sulphur compounds		n-Heptacosane	56
				Sylvestrene	56
Alcohols				Vanillin	56
		Hydrogen sulphide	56, 227	Furan	56, 227
Methyl	56, 225			Methylfuran	227
Ethyl	56, 226	Methanethiol	56, 227		
Furfuryl	56	Methyl sulphide	56, 227		
		2-Furylmethanethiol	56		
Phenols					
Phenol	56				
Cresols	56				
Quinol	56				
Resorcinol	56				
Eugenol	56				
Guaiacol	56				
2-Methoxy-4-vinylphenol	56				

Roast coffee contains 2×10^{-6} part of the aroma essence. The aqueous distillate of odoriferous compounds from coffee, after extraction of esters and drying, makes up 0.1% of the initial roast coffee. The coffee aroma essence contained mainly aldehydes and sulphur compounds, had a comparatively low solubility in water, and was readily oxidised in the air. It had a strong odour and gave clear yellow-green solutions in water. When sufficiently diluted with air it reproduced the aroma of coffee. The aroma of the coffee essence depended greatly on the type of coffee. The results of Zlatkis and Sivetz' chromatographic analysis of the coffee essence aroma [226] are given in Table 22.

Acetic acid (30%) and propionic acid (5%) were isolated from the distillate; the residue boiled at 90° (1 mm), and the compounds indicated in Table 21 were identified in it by gas chromatography [226]. Ketones and aldehydes containing six carbon atoms were also observed, as well as unidentified furfural derivatives. Zlatkis and Sivetz also indicate that the number of compounds present is probably far greater, since the odour of the compounds issuing from the chromatograph varied widely; for example, a pyridine-like odour was recorded, and also the sharp odour of organic acids.

The composition of the organic acids in coffee and its substitutes (barley, rye, and chicory) was studied by Schormüller *et al.* [229]; Table 23 gives their results for roast coffee. The volatile acids indicated in Table 23 undoubtedly play a part in the aroma of coffee, while the non-volatile acids affect its taste.

Several workers have attempted to reproduce the aromas of coffee and cocoa; thus in 1958 Rusoff patented the "synthesis" of the aroma of cocoa by the Maillard reaction, by heating plant and animal protein hydrolysates with sugars [230].

Meyer has reported [56] imitation of the aroma of coffee in the American food industry by using an artificial mixture comprising 10% of 2-furylmethanethiol, 3% of ethylvanillin, and 87% of an unspecified solvent. An artificial mixture reproducing the aroma of coffee has recently been developed at the Ukrainian Scientific Research Institute of the Food Industry [231]; this mixture contains furfural, methanethiol, valeraldehyde, isovaleric acid, 2-furylmethanethiol, guaiacol, quinol, and soyabean oil. Addition of 1 part of this mixture to 10 000 parts of chicory and barley malt extract gives the aroms of natural coffee.

TABLE 22. Analysis of aromatic coffee essence.

Compound	Content, wt. %	Compound	Content, wt. %
Acetaldehyde	19.9	Pentadiene	3.0
Acetone	18.7	Butanone	2.3
Biacetyl	7.5	C_4–C_7 alkanes and alkenes	2.0
n-Valeraldehyde	7.3	Methyl acetate	1.7
α-Methylbutyraldehyde	6.8	Methyl sulphide	1.0
Isovaleraldehyde	5.0	n-Butyraldehyde	0.7
Methylfuran	4.7	Ethyl formate	0.3
Propionaldehyde	4.5	Carbon disulphide	0.2
Methyl formate	4.0	Methanol	0.2
Carbon dioxide	3.8	Methanethiol	0.1
Furan	3.2	Thiophen	0.1
Isobutyraldehyde	3.0		

TABLE 23. Content of organic acids in roast coffee.

Acid	Content, mg (100 g)$^{-1}$	Percentage of total acidity	Acid	Content, mg (100 g)$^{-1}$	Percentage of total acidity
Formic	46.0	1.0	Lactic	437.5	9.3
Acetic	936.0	20.0	Succinic	283.0	6.0
Propionic	22.0	0.5	Malic	495.8	10.6
n-Butyric	35.0	0.7	Tartaric	9.0	0.2
n-Valeric	40.8	0.9	Citric	2200.0	47.0
Hexanoic	46.4	1.0	Fumaric	4.3	0.1
Octanoic	28.8	0.6	α-Oxoglutaric	20.0	0.4
			Pyruvic	77.5	1.7

VI. THE ODOUR OF MEAT AND FISH PRODUCTS

The chemical investigation of the aromas of meat and fish is far from complete, and there are very few published data.

The Aroma of Meat

The substances found in the odour of cooked meat are listed in Table 24.

Unfortunately, there are practically no data on the quantitative contents of these compounds. It is known only that, after beef has been cooked for 3 h, the broth contains 6–8 mg of hydrogen sulphide per kilogramme of meat [233], and that 79% of this hydrogen sulphide is oxidised on storage for 48 h. [232]

All workers agree that sulphur compounds and carbonyl compounds are important constituents of "meaty" odours. This cannot be said of fatty acids nor, apparently, of ammonia, since removal of the latter strengthens the odour of chicken broth [232].

During 1960–1962 it was shown by Hornstein [237,238] and by Batzer [239–241] that the phosphorus-containing glycoprotein fraction isolated from the dialysate of the aqueous extract of raw meat is a precursor of the odour of heated defatted meat. This fraction is very unstable on storage, even in a vacuum. Inosinic acid, hypoxanthine, inosine, glucose, and the amino-acids proline, isoleucine, leucine, valine, serine, and α- and β-alanine have been found as constituents of the glycoproteins. [240] Appropriate heating of the isolated fraction or a mixture of the above compounds gives the aroma of boiled or broiled meat, practically identical for beef, pork, and chicken meat. It is thought that the odour arises because of reaction between the amino-acids and the carbohydrates, for instance by a Maillard-type reaction. The absence from the glycoprotein hydrolysate of sulphur-containing amino-acids, which are precursors of the important sulphur-containing ingredients of meaty aromas, is surprising; possibly they have simply not been isolated.

TABLE 24. Compounds found in the odour of cooked meat.

Class	Compounds	Ref.
	ammonia	232, 233
Aldehydes	acetaldehydes, propionaldehyde, isobutyraldehyde, isovaleraldehyde	233–235
Ketones	acetone, butanone, acetoin, biacetyl	233–236, 236a
Sulphur compounds	hydrogen sulphide, methanethiol, ethanethiol, methyl sulphide	233–235
Fatty acids	formic, acetic, propionic, butyric, isobutyric	233

It is thus seen that fat-free meat has the same aroma irrespective of its type. The specific odours which distinguish different types of meat are thought by many to be related to the composition of the fats and their oxidation on heating[242]. Thus Hornstein and Crawe have found[238] that, when heated in a vacuum at 100°, beef fat acquires a sweet apple-like odour, and pork fat a pungent cheese-like odour[238]. These workers also investigated the composition of the carbonyl compounds isolated from fats heated in air at 100° (Table 25).

The volatile compounds of pork fat contain several times the quantity of carbonyl compounds, particularly hexanal, found with beef fat. These quantitative differences undoubtedly depend on the unsaturated acid content of the fats, and must play a part in the specificity of odour of different types of meat.

Apparently the full meaty odour and taste require the presence, in addition to the substances involved in producing the odour, of sodium *L*-monoglutamate[243], the effect of which is greatest in the pH range 5–6.5, where it exists as the glutamate ion $^{-}OCOCH(NH_3^+)CH_2CH_2COO^-$, responsible for the taste[244]. Sodium glutamate is widely used in a concentration of 0.1–0.5% to improve the taste of meat and vegetable dishes[245–248].

Unlike the meaty aroma, the odour of meat hydrolysates is due to amino-acid hydrolysis products, primarily α-oxobutyric acid produced from threonine[249–251].

Many studies have been made of the undesirable flavours and odours in fresh and prepared meat. Several unpleasant odours of fresh meat have been found to be associated with the animal feed[252,253].

γ-Irradiation is widely used for the sterilisation of meat products, and hence the nature and source of the unpleasant odours thereby produced have also been investigated. Among constituents of these odours have been identified amines, including methylamine and ethylamine[254], carbonyl compounds (n-alkanals, alk-2-enals, and ketones)[255–257], peroxides[257], and sulphur compounds (hydrogen sulphide, methanethiol, and methional)[257–259]. It should be noted that the carbonyl compounds produced when muscle tissue and fat are irradiated are greatly different[255,256]. Methional is not produced directly from methionine in γ-irradiated raw meat, but as the result of peroxide-initiated radical addition of methanethiol to acrylaldehyde[257,259]. By adding DL-methionine and glutathione labelled with ^{35}S to the meat before irradiation, Batzer and his coworkers established that most of the methanethiol is formed directly from methionine, and hydrogen sulphide from both compounds, though in small amounts[260].

TABLE 25. Carbonyl compounds isolated from fats heated in air at 100°.

Fraction	Beef fat		Pork fat	
	compounds	concn., mmole × ×(10g)$^{-1}$	compounds	concn., mmole × ×(10g)$^{-1}$
Volatile fraction	acetone, propanal	0.039	acetone, propanal, hexanal, octanal, nonanal	0.27
	acetaldehyde and 2-enals	0.072	acetaldehyde and C_7–C_{11} 2-enals deca-2,4-dienal	0.06
Fraction obtained by steam distillation	hexanal, nonanal	0.070	hexanal, octanal, nonanal, undecanal	0.24
	C_7–C_{11} 2-enals	0.028	C_7–C_{11} 2-enals	0.12
	deca-2,4-dienal	0.021	C_7, C_9, and C_{10} 2,4-dienals	0.083

The deterioration of raw and cooked meat on storage has several causes and is accompanied by the production of various odours. Decomposition of proteins and fats in raw meat is mainly due to the action of microorganisms. The main participants in the formation of the odour of bad raw meat are amines (predominantly trimethylamine) and aliphatic acids from acetic to octanoic (mainly hexanoic acid)[261]. Determination of ammonia in the meat is recognised as the best method for detecting the initial stages in decay[262,263]. Biacetyl and acetoin have also been detected in the odour of putrefying meat[264]. The microbiological decomposition of amino-acids in dehydrated conserved pork at elevated temperature produces also acetaldehyde and ammonia[265]. Other processes underlie the deterioration of cooked meat. Here the thiobarbituric method has shown that tissue lipids are rapidly oxidised, with the formation of unpleasant odours and tastes[266]. Malonaldehyde has been identified as a component of the rancid odour of cooked meat[267].

Because of the absence of data on the quantitative proportions of the ingredients of meaty odours, it is difficult to expect production of the aromas on mixing the constituents. The only attempt produced an odour only faintly resembling a meaty odour[236]. A more logical and promising method for creating this odour is to use appropriate precursors; thus May and his coworkers carried out a model Maillard reaction by heating an aqueous solution of cysteine and one or more other amino-acids with carbonyl compounds or compounds producing them[268–270]. Racemic amino-acids can be used instead of the L-isomers, or else derivatives (salts, esters, or oligopeptides) which yield the amino-acids under the experimental conditions. Carbohydrates were initially employed as carbonyl compounds[268], and it was then found possible to replace these by simpler aldehydes (propionaldehyde or glyceraldehyde)[269] or even furan derivatives[270].

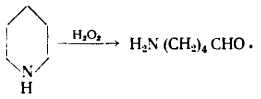
Imitation of the meaty odour by a single chemical compound is a very alluring prospect. It was long thought that methional could produce a brothlike odour[271], although all attempts to achieve this were unsuccessful. It was shown in 1959 that methional purified by gas chromatography apparently does not have this odour[272]. Serious attention is merited by a patent[273] for the production of a meaty aroma in edible compositions by the addition of 0.005–0.06 wt. % of a derivative of mercaptoacetaldehyde, which is a decomposition product of cysteine, a constituent of all suggested precursors. These compounds can also be used in admixture with sodium glutamate or other odoriferous or taste-producing compounds.

The Aroma of Fish

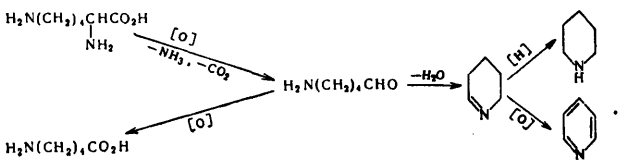
The aroma of fish products differs considerably from meaty odours. Studies of fish odours were mainly carried out on fresh and stored fish, and only since 1959 have investigations appeared on the odour of heated fish.

Obata and his coworkers showed that piperidine, pyridine, and their oxidation products δ-aminovaleraldehyde and δ-aminovaleric acid, which are found in the epidermal slime of fish, cause the odour of fresh fish[274]. They were

able to imitate the odour of fresh freshwater fish by oxidising piperidine to δ-aminovaleraldehyde with 10% hydrogen peroxide:



Addition of trimethylamine to the mixture gives the odour of fresh sea fish, which accords well with the high content of trimethylamine in sea fish [275]. The source of the compounds found by the Japanese chemists is apparently lysine, which undergoes chemical or microbiological decomposition [276]. The following mechanism could be suggested for their formation



Analogous processes occur to an even greater extent when fish is stored; thus the Japanese workers established the presence of δ-aminovaleric acid in slightly stale fish, and were able to confirm experimentally its importance in formation of the corresponding odour [274]. Methanethiol and indole were identified in fish which had deteriorated further. Amano has shown that green meat in frozen swordfish has a high concentration (12 mg per 100 mg of fish) of isovaleric acid, which is the cause of the unpleasant odour of such fish [277]. Piperidine and pyrrolidine have also been found in stale fish [278]. Hughes has shown that in stored herring trimethylamine *N*-oxide decomposes, producing mainly ammonia and trimethylamine [279]. Many carbonyl compounds have been identified in the autoxidation of the fat of salmon, which are also obtained in the oxidation of other fats [280].

Quantitative determination of the substances formed provides an objective evaluation of the freshness of fish [281-283]. The concentration of lower carbonyl compounds in fish increases linearly with its storage time. The content of higher carbonyl compounds is a maximum after 8–11 days, [284] which accords well with organoleptic analysis of the freshness of fish [285]. The content of volatile acids (formic, acetic) can also be used as a criterion of the quality of fish [286].

The odour of dried fish contains the same constituents as that of fresh and bad fish, but apparently in different proportions. Thus ammonia, trimethylamine, pyridine, piperidine, and the five fatty acids formic, acetic, propionic, butyric, and lauric have been found in a methanolic extract of katsuobushi (fish dried in pieces) [287].

There is least published information of all on the chemical composition of the odours of prepared fish — only Hughes' studies on cooked herring, which showed its odour to contain ammonia, dimethylamine, trimethylamine, methylamine, acetaldehyde, propionaldehyde, isobutyraldehyde, α-methylbutyraldehyde, and acetone [279,288]. Steam distillation from fillet of haddock has also given α-hydroxycarbonyl and dicarbonyl compounds having 2–4 carbon atoms [289], possibly acetoin and biacetyl.

When fish meat is treated with steam under pressure, the trimethylamine *N*-oxide decomposes:

$$(CH_3)_3NO \rightarrow CH_2O + (CH_3)_2NH.$$

Both these products have been detected in tinned fish, the concentration of dimethylamine being fairly high and proportional to the concentration of trimethylamine *N*-oxide in the fresh fish meat [290].

There are also very few data on the sources and precursors of the odour of prepared fish. It is thought that reactions of carbohydrates with amines and amino-acids play an important part in the formation of the aroma of fish in this case [291].

The flavour of fish products can be improved by adding sodium glutamate in a concentration of 0.15–1%, depending on the type of product [292,293]. Thus unlike the meaty odour, where sulphur compounds are the most important, the odour of prepared fish is due mainly to the presence of nitrogen compounds, particularly methylamines. Carbonyl compounds are important constituents of both types of odour.

The Odour of Smoked Products

Smoked meat and fish products have special odours of their own, produced with the participation of the curing-house smoke, which contains organic acids, phenols, and mono- and poly-carbonyl compounds [294,295]; these are absorbed by the product, where they may also undergo various reactions. Hardly any work has been done on the compounds causing the odour of smoked products. Only in 1960 did Yuditskaya and Lebedeva show that phenol, guaiacol, and *m*- and *o*-cresols are always present in fish smoked by any method [296]; depending on the method of smoking, *p*-cresol, pyrogallol methyl ethers, and two unidentified phenols may also be present. The composition of the phenols changes on storage. In meat products a higher content of phenols corresponds with a better organoleptic evaluation of the product [297]. Despite the poor knowledge of the composition of the odours of smoked products, they have been successfully imitated. It has been proposed to use a fraction of the dry distillation products of wood to imitate the odour of smoked products generally [298], and a mixture obtained by heating this fraction with cysteine and other amino-acids (or protein hydrolysates) to imitate the odour of ham [299].

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The aromas of milk, cream, butter, cheese, bread, meat, coffee, and cocoa are found to be very similar in composition, containing the same classes of chemical compounds — aldehydes, ketones, alcohols, esters, aliphatic acids, amines, heterocyclic compounds (furan and its derivatives), and sulphur compounds. Certain aldehydes and ketones are present in all the food products. However, apparently far from all the substances found in the aroma of a food product are necessary for its reproduction. For example, methanol and ethanol, which are present in the aroma of all food products, and carbon dioxide, which is found in the volatile constituents of coffee, can hardly play any substantial part. From the substances responsible for flavours in milk (Table 2) it is readily seen that the specific aroma of each food product is probably determined on the one hand by the different proportions of the components, and on the other by the presence of certain

compounds which, on the general background of the other volatile substances, produce definite and characteristic shades of flavour.

The great similarity in the various odoriferous compositions suggests the existence of general routes by which the volatile components are produced. Some of these can even be named — enzymic splitting of fats and proteins, autoxidation of fats, and the Maillard reaction. Study of these reactions is extremely important for investigating the processes by which the odoriferous compounds are produced, so that they may be utilised practically. Very important also is knowledge of the actual precursors of the aroma of a given product. The reproduction of an odour by using such precursors is beginning to be used outside the U. S. S. R.; for instance, the aroma of fresh bananas is given to preserved bananas by utilising the decomposition of three precursors by means of an enzyme obtained from fresh bananas.

Claims have recently been made in the U. S. A. to the imitation of the odours of cheese, butter, and milk with the use of lipolytic enzymes.

From the data presented in this review, it may be affirmed that knowledge of the chemistry of the odour of food products can not only considerably improve the aroma of commercial food products, but can also, in the not too distant future, provide from non-food starting materials synthetic food which is as good as, or in some cases even better than, natural food products, in respect of flavour and nutritional qualities.

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THE THERMODYNAMICS OF PROCESSES OF NEW-PHASE FORMATION

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1. INTRODUCTION

The theoretical and experimental study of processes of new-phase formation and the associated metastable states has been the subject of many papers, to which extensive reference has been made in a number of books, reviews, and symposia[1-12]. The great majority of these papers contain a discussion of the kinetics of the phase change, but all necessarily deal with the thermodynamics of the process, usually employed to estimate the work of forming a nucleus and its magnitude. This part of the theory has seemed most straightforward and has been based on the relationships given by Gibbs[13] and Kelvin[14], used in unchanged form by Volmer[3] and Becker and Döring[15], and transferred continuously from one paper to another, strengthening belief in their general applicability and triviality.

Studies carried out in the 1950's on the thermodynamics of microheterogeneous systems[16-30] showed, however, that the question is not so simple. The efforts of thermodynamicists were turned first towards a thorough analysis and correct interpretation of Gibbs' theory of surface phenomena and second to the development of this theory with the aim of deriving thermodynamic relationships for curved surfaces. Most of the results obtained concerned the dependence of surface tension on the curvature of the surface[17-27].

It was found that despite agreement with experiment[8,31-34] (theories of) the kinetics of phase changes include a number of unjustifiably crude assumptions which make no allowance for the properties of objects as small as the nuclei of new phases. The error involved in equating the properties of a nucleus to the properties of a macroscopic phase was pointed out at an early date by a number of authors, including Frenkel'[35], who continued, however, to assume that the surface tension and density of a nucleus were constant. After rigorous thermodynamic formulae describing the dependence of surface tension on the size of the nucleus[17] had been obtained, attempts were made[8,32] to introduce this dependence into the Becker–Döring kinetic equation[15]. The results obtained showed less satisfactory agreement with experiment than the original equation, and certain authors[8,10,36] preferred to continue within the framework of the "classical" theory making no allowance for the thermodynamic corrections.

This lack of success should not arouse scepticism towards rigorous thermodynamic relationships. As pointed out correctly by Buff and Kirkwood[20], unilateral allowance for the dependence of the surface tension on the curvature of the surface in equations based on the assumption that this quantity is constant may lead not to improvement but to worsening of the theory. To obtain a correct result it is necessary to make a systematic reexamination of the entire theory allowing not only for the dependence of surface tension on the size of the nucleus but also for the corresponding dependences of other thermodynamic parameters (density, composition, etc.).

Thus one of the problems in the thermodynamics of new-phase formation concerns the rigorous thermodynamic relationships characterising the equilibrium properties of small objects.

Another problem raised by the success of the thermodynamics of curved surfaces concerns more rigorous allowance for the physical conditions under which the process takes place, in calculating the work of formation of a nucleus. The result obtained by Gibbs is strictly applicable only to an infinitely large system, when the conditions under which the process takes place have no significance. When applied to real finite systems, this result becomes approximate and it is necessary to consider the corrections, whose magnitude depends on the conditions under which the process takes place.

In the present paper we shall have both of these problems in mind when discussing processes of new-phase formation.

The following symbols are used:

A = area of interface,
F = free energy,
H = enthalpy,
m_i = number of moles of the i-th component,
P = pressure,
R = the gas constant,
r = radius of curvature of the interface,
S = entropy,
s_i = partial molar entropy of the i-th component,
T = absolute temperature,
U = total internal energy,
V = volume,
v = molar volume,
v_i = partial molar volume of the i-th component,
W = work of formation of a new phase,
μ_i = chemical potential of the i-th component,
σ = surface tension,
Φ = Gibbs thermodynamic potential.

The superscript (1) indicates that the quantity belongs to the internal phase (nucleus) and the superscript (2) the external phase (medium).

2. TWO THERMODYNAMIC TREATMENTS OF METASTABLE STATES

Stable equilibrium in a multicomponent system is characterised by a minimum total internal energy U of the system at constant entropy S, volume V, and mass of the com-

ponents m_i ($i = 1, 2, \ldots$), so that when the system departs from the equilibrium state the condition

$$(\Delta U)_{S,V,m_1,m_2,\ldots} > 0 \qquad (1)$$

should be satisfied.

According to Gibbs, it is necessary to distinguish two types of stability in homogeneous systems: stability relative to continuous changes in the given phase and stability relative to the formation of new phases (in the macroscopic sense). In the first case condition (1) applies to infinitely small changes and in the second case to finite changes.

Phases which are unstable with respect to infinitely small changes cannot exist, so that the term "stable state" is usually understood to mean a state stable relative to continuous changes. In a detailed treatment of condition (1), Gibbs obtained an inequality characterising the stability of a homogeneous system:

$$dTdS - dPdV + \sum_i d\mu_i\, dm_i > 0. \qquad (2)$$

This inequality leads to the familiar particular stability conditions characterising the mutual change in temperature and entropy, pressure and volume, and chemical potentials and masses of the components.

While completely stable relative to continuous changes and satisfying inequality (2), a phase of large dimensions may be unstable with respect to the formation of another macroscopic phase, so that inequality (1) is not fulfilled for certain finite changes. If, however, condition (1) is fulfilled for any finite changes, the phase is also completely stable with respect to the formation of new phases. In the first case we speak of the metastable state and in the second of the stable state of the phase.

When the energies of the phases are equal, the left-hand side of (1) becomes zero, with the production of an indifferent equilibrium corresponding to the boundary of stability relative to finite changes. Since these phases may coexist, the two-phase equilibrium curve or surface on the equilibrium diagram of the system (binodal) is also the curve or surface bounding the stable and metastable states (curve AKB in Fig. 1, phases A and B coexist).

The boundary of stability relative to continuous changes is reached when the left-hand side of (2) becomes zero and the curve or surface (spinodal) corresponding to this condition defines the stable and unstable states on the equilibrium diagram of the system (curve CKD in Fig. 1). At the critical point the stability boundaries of both types are reached and the binodal and spinodal touch one another. It follows from the thermodynamic theory of critical phenomena [37,38] that the curvature of the spinodal at the critical point is greater (by a factor of 3 in the case of binary systems, and of 1–3 in the case of ternary systems) than that of the binodal, so that the former lies inside the latter. With this mutual disposition of binodal and spinodal, the region between them corresponds to metastable states, from the definition of the latter.

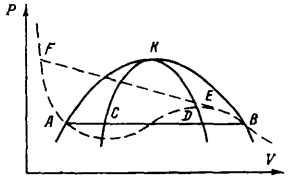

Fig. 1. Two-phase equilibrium in a one-component system: AKB-binodal, CKD-spinodal.

Thus the thermodynamics of macroheterogeneous equilibria leads logically to the existence of stable, metastable, and unstable states, establishes the position of the metastable range on the equilibrium diagram of a system, and defines the relative part played by the metastable and unstable regions in the neighbourhood of the critical point. In the general case, at a distance from the critical point, the thermodynamics of macroheterogeneous systems give no information on the width of the metastable range, apart from the fact that it is finite.

In this case another approach, provided by the thermodynamics of microheterogeneous systems, is extremely useful. Since the conditions of equilibrium for a finely-divided substance require that allowance be made for surface phenomena and curvature of the surface and hence differ from the corresponding conditions for macroscopic phases, it may be assumed that to each metastable state there corresponds an equilibrium with a particle of new phase, of definite dimensions. A characteristic feature of this equilibrium is that one of the phases lies in the metastable range and the other in the stable range, whereas in equilibrium between large masses the figurative points of the phases lie on the binodal. Thus isothermal compression of the equilibrium vapour B (Fig. 1) leads to the production of a metastable state E, which can be regarded as existing in equilibrium with a small drop of liquid in the state F, exhibiting an increased vapour pressure. The pressure inside the drop should exceed this pressure and the node FE will not now be horizontal.

In this treatment the width of the metastable range should be determined by the change in the dimensions of the equilibrium nucleus of the new phase from zero to macroscopic values and by the corresponding increase in the work W of formation of the nucleus on going from the spinodal to the binodal; this would correspond to complete consistency in the theories of macro- and micro-heterogeneous equilibria.

The theoretical results obtained in this field for binary systems are somewhat contradictory. According to Becker [39], W increases markedly as the binodal is approached; this indicates an increase in the stability of the system and agrees completely with the thermodynamics of macro-phases. Cahn and Hilliard [29] concluded that W becomes zero when the spinodal is reached, but they also extended this result to the unstable range. Some authors [8,40] postulate the existence of an energy barrier on the spinodal, *i.e.* they consider that W differs from zero.

In Section 5 we shall show that the use of rigorous thermodynamic formulae leads to complete consistency between the thermodynamics of microheterogeneous systems and general thermodynamic concepts. Before proceeding to a discussion of this question, however, it is necessary to become familiar with the thermodynamic properties of the nuclei of new phases and methods for calculating the work of their formation.

3. THE CONCEPT OF THE NUCLEUS OF A NEW PHASE

Volmer [3] gave two definitions of the nucleus of a new phase. According to the first, the nucleus is a region in the new phase, in chemical equilibrium with the medium

and hence satisfying the condition that the chemical potentials of the nucleus and medium are equal. The second definition, given by Volmer in an examination of drops of liquid in a vapour, relates the concept of the nucleus to the maximum work of its formation from the molecules of the old phase. Volmer considered that the equilibrium condition determines completely the dimensions of the new phase, but this is not always so. The two definitions become equivalent if the term "nucleus" is understood to mean the *minimal* accumulation of new phase in equilibrium with the medium [41].

From Volmer's definitions, which have been adopted by most authors, it follows that he understood the term "nucleus" to mean a new formation of definite (critical) dimensions. A number of authors, however, following Frenkel' [35], use this term in a wider sense and understand by the term "nucleus" any (not necessarily equilibrium) formation consisting of new phase. The same term is sometimes used [42-44] to denote regions of the new phase which have not yet reached critical dimensions. Subsequently, therefore, we shall speak of "equilibrium nuclei" if we are dealing with Gibbs–Volmer nuclei and simply "nuclei" if the dimensions of the region of new phase are not of fundamental importance.

Having become familiar with the terminology, we must decide upon a method for the thermodynamic description of regions of new phases and particularly a method for defining their dimensions. Since the nucleus may be very small, it is necessary, for an accurate characterisation of its extent, to define a closed geometric surface whose dimensions change regularly with change in the physical state of the system under equilibrium conditions. The choice of this surface is not unique. Following Gibbs, we can take it to be the surface whose tension satisfies the condition (for spherical surfaces):

$$P^{(1)} - P^{(2)} = \frac{2\sigma}{r}. \qquad (3)$$

Having defined the geometric surface and mentally extended to this surface the external phase with all its macroscopic properties, we obtain certain excesses (from the side of the external phase) of extensive properties and relate these to the separating surface. If we now combine the separating surface with the total mass inside it, we obtain a complex which can be called the nucleus of the new phase (in the broad sense). Thus the mental operation involves the replacement of a real system consisting of two phases and a surface layer, or of a surface layer and an external phase (if an internal phase as such does not exist), by two substances — a nucleus and a medium — with a clearly-defined boundary between them.

As already noted, macro-phase properties were originally attributed to the nuclei. While rejecting this mechanistic viewpoint, we can retain its rational core and assume that the nucleus exists in equilibrium within itself. This makes it possible to use (possibly in a quasi-thermodynamic sense) the fundamental equation characterising the state of internal equilibrium for the complex being considered:

$$Ad\sigma - V^{(1)}dP^{(1)} + S^{(1)}dT^{(1)} + \sum_i m_i^{(1)} d\mu_i^{(1)} = 0, \qquad (4)$$

where A is the area of the tension surface and the superscript (1) indicates that the quantity refers to the nucleus. It should be remembered that the quantities $S^{(1)}$ and $m_i^{(1)}$ by definition, include not only the entropy and masses of the components inside the volume $V^{(1)}$ but also the excesses of these quantities from the external phase side. Thus when $V^{(1)}$ and A become zero, $S^{(1)}$ and $m_i^{(1)}$ still retain finite values.

Eqn. (4) does not include any assumptions regarding the equilibrium between the nucleus and the medium, and can be used to characterise nuclei of any dimensions. For crystalline nuclei the quantities σ and r should be understood in accordance with the expressions

$$\sigma \equiv \frac{1}{A}\left(\sum_j \sigma_j A_j + \sum_k \tau_k l_k\right) \qquad (5)$$

and

$$r \equiv \frac{3V^{(1)}}{A}, \qquad (6)$$

where σ_j and A_j are the surface tension and area of the j-th face, and τ_k and l_k the linear tension and length of the k-th edge. The concept of a surface of tension also retains its meaning in this case [45].

4. CALCULATION OF THE WORK OF FORMATION OF A NEW PHASE BY MEANS OF THERMODYNAMIC POTENTIALS

The calculation of the work of formation of new phases plays an extremely important part in the theory of phase processes. In the first place, a knowledge of this quantity makes it possible to reach conclusions regarding the statistical distribution with respect to dimensions of nuclei, produced by fluctuations:

$$n = n_0 e^{-\frac{W}{kT}}, \qquad (7)$$

where n is the number of nuclei of given dimensions and n_0 is a slowly-changing function of W. In the second place, a knowledge of the maximal work of formation of the nucleus is necessary in order to establish the kinetics of the phase change. This quantity, together with the activation energy of the diffusion process Q, appears in the familiar kinetic equation

$$J = Ne^{-\frac{W+Q}{kT}}, \qquad (8)$$

where J is the rate of production of new phase and N a slight function of W.

The magnitude of the work of formation of the new phase depends on the mechanism of the process and the conditions under which it takes place. Two mechanisms are usually distinguished: homogeneous (spontaneous), when the nucleation of the new phase takes place in the bulk of the old phase, and heterogeneous, when this process takes place at the phase boundary.

Thermodynamic calculation [3,13] has shown that the work expended in the formation of an equilibrium nucleus by a heterogeneous mechanism is less than that for a homogeneous mechanism, and on this basis Volmer [3] concluded that heterogeneous processes predominate greatly in natural and laboratory conditions. Later studies showed that the homogeneous formation of new phases also plays an important part. In particular, it was found that not all heterogeneous impurities can act as centres for condensation or crystallisation [9,34], so that the presence of foreign particles in a system does not provide proof of a heterogeneous phase-change mechanism.

Moreover, observation of the crystallisation of small drops established the existence of supersaturations much greater than those for large masses. Thus drops of water with dimensions of 1–20 μm could be supercooled to

-40°,[11,46-50] whereas supercooling in a large mass of water did not even reach -20°. High supersaturations were observed for drops of organic liquids[50] and, more particularly, for metals[8,51,52]. For example, drops of Au with dimensions 10–15 μm can be supercooled by 230 deg, whereas the supercooling for a large mass amounts to only 2–3 deg; drops of Pt can be supercooled by 370 deg, etc. On the basis of these data it was concluded that the nucleation of new phases in finely-divided substances takes place by a homogeneous mechanism[8,11,52,53]. Thus it must be assumed that both phase-change mechanisms are of practical importance and thus deserve detailed study.

An extremely convenient (but not unique) method for finding the work of formation of new phases under different conditions involves the use of thermodynamic potentials. Of these, the five most familiar are: the energy U, enthalpy H, free energy F, Gibbs thermodynamic potential Φ, and potential Ω. For homogeneous systems the change in each of these potentials under definite conditions gives the magnitude of the "useful" work W:

$$W = \Delta U \text{ for constant } S,\ V,\ m_1,\ m_2,\ \ldots. \quad (9)$$
$$W = \Delta H \text{ for constant } S,\ P,\ m_1,\ m_2,\ \ldots. \quad (10)$$
$$W = \Delta F \text{ for constant } T,\ V,\ m_1,\ m_2,\ \ldots. \quad (11)$$
$$W = \Delta\Phi \text{ for constant } T,\ P,\ m_1,\ m_2,\ \ldots. \quad (12)$$
$$W = \Delta\Omega \text{ for constant } T,\ V,\ \mu_1,\ \mu_2,\ \ldots. \quad (13)$$

Since U, F, and Ω are defined in similar fashion for homogeneous and heterogeneous systems, expressions (9), (11), and (13) can also be applied without reservation to the processes of new-phase formation. Expressions (10) and (12) are applicable with the condition that the pressure in the system is constant, and it is known that this condition is not fulfilled for microheterogeneous systems. These expressions can also be used to calculate the work of formation of a nucleus, however, only if the external pressure is assumed to be constant and the corresponding thermodynamic functions for heterogeneous systems are defined in the same way as those used for homogeneous masses (see Section 5 for details).

Gibbs[13] considered the formation of an equilibrium nucleus in an infinite system and showed that the work necessary for this is equal to one-third of the surface energy of the nucleus. In the particular case of a homogeneous process

$$W = \frac{1}{3}\sigma A. \quad (14)$$

In the case of an infinite system, the conditions under which the process takes place are of no importance and any of the expressions (9)–(13) can be used to obtain (14). A difference appears only when the system is assumed to be finite. In practice this means that the volume and mass of the system per nucleus are not too large.

The effect of the conditions under which the process takes place on the work of formation of a new phase are almost independent of its mechanism and we shall examine this effect first of all for the case of homogeneous processes.

5. THE FORMATION OF A NEW PHASE UNDER ISOBARIC-ISOTHERMAL CONDITIONS

Let us consider the particular case of the homogeneous formation of a new phase under conditions of constant external pressure and temperature. In order to calculate the work of the process by Eqn. (12), it is necessary to find the values of the Gibbs potential for the original state, consisting of a homogeneous (metastable or unstable) medium, and the final state, which includes the nucleus and a metastable phase which generally speaking are not in equilibrium with one another. The energies of these two states are determined by the fundamental equations

$$U_{\text{hom}} = TS - PV + \sum_i \mu_i m_i \quad (15)$$

and

$$U_{\text{het}} = TS - P^{(1)}V^{(1)} - P^{(2)}V^{(2)} + \sigma A + \sum_i \mu_i^{(1)} m_i^{(1)} + \sum_i \mu_i^{(2)} m_i^{(2)}. \quad (16)$$

The Gibbs potential for the initial stage is by definition

$$\Phi_{\text{hom}} \equiv U_{\text{hom}} - TS + PV = \sum_i \mu_i m_i. \quad (17)$$

In exactly the same way it is necessary to determine this potential for the final state by putting P equal to the pressure of the external phase $P^{(2)}$:

$$\Phi_{\text{het}} \equiv U_{\text{het}} - TS + P^{(2)}V = (P^{(2)} - P^{(1)})V^{(1)} + \sigma A + \sum_i m_i^{(1)}\mu_i^{(1)} + \sum_i m_i^{(2)}\mu_i^{(2)}. \quad (18)$$

This definition is contrary to that generally accepted ($\Phi = \sum_i \mu_i m_i$), but without it expression (12) cannot be used.

The quantities $\mu_i^{(1)}$ and $\mu_i^{(2)}$ are equal in the case of equilibrium, but in any case they relate to different pressures $P^{(1)}$ and $P^{(2)}$. If we reduce $\mu_i^{(1)}$ to the value at $P^{(2)}$ using the formula

$$\mu_i^{(1)}(P^{(1)}) \simeq \mu_i^{(1)}(P^{(2)}) + v_i^{(1)}(P^{(1)} - P^{(2)}), \quad (19)$$

where $v_i^{(1)}$ is the partial molar volume of the i-th component in the new phase, Eqn. (18) acquires the shorter form

$$\Phi_{\text{het}} \simeq \sigma A + \sum_i m_i^{(1)}\mu_i^{(1)}(P^{(2)}) + \sum_i m_i^{(2)}\mu_i^{(2)}, \quad (20)$$

which has been used by Frenkel'[35] and many others. The disadvantages of this form are its approximate character and the fact that it contains the arbitrary quantity $\mu_i^{(1)}(P^{(2)})$.

Subtracting (17) from (18) and taking account of the conservation of mass ($m_i = m_i^{(1)} + m_i^{(2)}$), we obtain the work of formation of a nucleus under isobaric-isothermal conditions:

$$\Delta\Phi = (P^{(2)} - P^{(1)})V^{(1)} + \sigma A + \sum_i (\mu_i^{(1)} - \mu_i^{(2)}) m_i^{(1)} + \sum_i (\mu_i^{(2)} - \mu_i) m_i. \quad (21)$$

In order to study the dependence of $\Delta\Phi$ on the size of the nucleus, we differentiate the expression for $\Delta\Phi$, using the Gibbs–Duhem equation and Eqn. (4):

$$d\Delta\Phi = (P^{(2)} - P^{(1)})dV^{(1)} + \sigma dA + \sum_i (\mu_i^{(1)} - \mu_i^{(2)}) dm_i^{(1)}. \quad (22)$$

Assuming that $V^{(1)} = \frac{4}{3}\pi r^3$ and $A = 4\pi r^2$, we can readily show that when equilibrium conditions are established — chemical potentials equal and condition (3) satisfied — the expression (22) becomes zero. Substituting the same conditions in (21), we obtain the limiting value of $\Delta\Phi$, corresponding to the formation of a nucleus in equilibrium with the medium:

$$\Delta\Phi_0 = \frac{1}{3}\sigma A + \sum_i (\mu_i^{(2)} - \mu_i) m_i. \quad (23)$$

The difference $\mu_i^{(2)} - \mu_i$ shows the change in the chemical potentials during the formation of the nucleus. For an infinite system this difference is equal to zero and (23) reduces to the Gibbs formula (14).

In order to establish the type of extremum, we evaluate the second differential of $\Delta\Phi$, again taking account of (4):

$$(d^2\Delta\Phi)_0 = -8\pi\sigma(dr)^2 + \left[d\sigma\, dA - dP^{(1)}dV^{(1)} + \sum_i d\mu_i^{(1)}dm_i^{(1)}\right] + \left[\sum_i d\mu_i^{(2)}dm_i^{(2)}\right]. \quad (24)$$

The result obtained does not lead so obviously to a maximum as is generally assumed. Since allowance is made for the individual properties of the nucleus and the finite dimensions of the system, expression (24) contains, in addition to the first term, which is clearly negative, two further terms, in square brackets. The second of these, in accordance with condition (2) for constant T and P, is always positive, since the phase in equilibrium with the nucleus is stable (metastable). In analogous fashion the sign of the first term in square brackets characterises the internal stability of the nucleus: if the nucleus is stable, this term is positive, otherwise it is negative.

If the system is sufficiently large, so that the formation of a nucleus has almost no influence on its state, the second term in (23) and the third in (24) are very small. The fact that a maximum value of $\Delta\Phi$ exists then follows from Eqn. (23) itself, so that expression (24) should be negative and hence if the second term in (24) is also positive it should have an absolute magnitude which does not exceed that of the first term.

Thus analysis of (24) shows that the possibility of a positive sign for this expression and of a corresponding minimum value for $\Delta\Phi$ arises only when the absolute magnitude of the third term is sufficiently high. This is conceivable, in the first place, for relatively small systems, and in the second place only for multicomponent systems.

In the case of a one-component system, constant values of the external pressure and temperature correspond at the same time to a constant value for the chemical potential of the substance in the two phases, and (23) acquires the simpler form:

$$\Delta\Phi_0 = \frac{1}{3}\sigma A. \quad (25)$$

According to (25), the work of formation of an equilibrium nucleus is always positive and increases with increase in its dimensions. The upper limit of $\Delta\Phi_0$ is reached for almost complete conversion of the original mass into the new phase (if the quantity σ is to retain its significance, it may be assumed that the maximal amount of new phase formed is still surrounded by a film of the old phase, necessary for equilibrium). If the system is infinite, there is no upper limit for $\Delta\Phi_0$ ($\Delta\Phi_0 \to \infty$ as $r \to \infty$). The lower limit is reached when A becomes zero, so that the work of formation of the equilibrium nucleus also becomes equal to zero ($\Delta\Phi_0 \to 0$ as $r \to 0$). This should evidently correspond to limiting supersaturation.

6. LIMITING SUPERSATURATION

In the literature on the formation of new phases, extensive use is made of the Kelvin, Thomson, and Ostwald–Freundlich relationships which characterise the equilibrium between small particles and a medium. Kelvin's formula describes the change in vapour pressure for isothermal curvature of the surface:

$$\ln\frac{P^{(2)}}{P_\infty^{(2)}} = \frac{2\sigma v^{(1)}}{rRT}, \quad (26)$$

where $P_\infty^{(2)}$ and $P^{(2)}$ are the pressures above planar and curved surfaces respectively and $v^{(1)}$ is the molar volume of the internal phase.

The Ostwald–Freundlich equation gives an analogous relationship for the change in solubility:

$$\ln\frac{x^{(2)}}{x_\infty^{(2)}} = \frac{2\sigma v^{(1)}}{rRT}, \quad (27)$$

where $x_\infty^{(2)}$ and $x^{(2)}$ are the solubilities of the substance in solution above planar and curved surfaces respectively.

Thomson's equation for isobaric superheating or supercooling ΔT with curvature of a planar surface has a slightly different form

$$\frac{\Delta T}{T} = \frac{2\sigma v^{(1)}}{rL}, \quad (28)$$

where L is the heat of the phase change.

All three equations are used to examine the phenomena of condensation and crystallisation in order to calculate the dimensions of the equilibrium nucleus for a given supersaturation and, in the final analysis, to calculate the work of formation of the nucleus. It follows from Eqns. (26)–(28) that the limiting supersaturation, corresponding to the condition $r = 0$, is infinite and hence unattainable. This conclusion clearly contradicts general thermodynamic theories of the finite nature of the metastable range and also experimental data, according to which a phase change is observed when a certain finite supersaturation is reached.

Several suggestions have been made in order to explain this contradiction. In the first place, Ostwald pointed out that the experimentally observed critical supersaturation is not the limiting supersaturation, but corresponds to an increase in the rate of phase transformation to an experimentally-observable value, which does not provide proof for the finite character of the limiting supersaturation. Nevertheless at the present time it is assumed that the limiting supersaturation is finite. Some authors suggest that the limiting supersaturation corresponds to the minimal possible dimensions of the new phase (elementary crystallites [54,55], minimal molecular associates [35]) and, on the basis of these minimal dimensions, they calculate the magnitude of the limiting supersaturation from Eqns. (26)–(28). [35,56,57] On the other hand, it is pointed out that Eqns. (26)–(28) lose their validity when the values of r reached are so small that thermodynamic consideration of the particle becomes unjustified. On the basis of this viewpoint, it is assumed that the limit of applicability of the Ostwald–Freundlich equation corresponds to the dimensions of colloidal particles (50 mμm), which also correspond to limiting supersaturation [58]. According to Rodebush [59,60], Kelvin's equation can have a meaning only when $r > 10^{-7}$ cm, not only because the surface tension for smaller dimensions is not constant, but also because, for smaller dimensions of the molecular aggregates, the vapour pressure of the drop as such does not exist, since these very small molecular aggregates themselves begin to play a significant part in the establishment of the equilibrium pressure.

Thus most authors relate the limiting supersaturation to a finite value of r. In some cases, it is true, this value is assumed to be very small, and it is usually considered that the dimensions of the minimal nucleus coincide with the dimensions of a single molecule [61]. Calculations carried out from formulae (26)–(28) lead to a higher value of r, corresponding to the presence of several [56] or several dozen [62,63] molecules in the nucleus.

The conclusion regarding a finite minimum value of r, although contrary to general thermodynamic theories of the limit of stability to continuous changes, is quite understandable from the molecular viewpoint. Moreover, this conclusion agrees with experimental data on the finite nature of limiting supersaturation and in principle does not contradict Eqns. (26)–(28). When these equations are used, however, two features are generally overlooked.

In the first place, Eqns. (26)–(28) are approximate relationships, applicable only for large values of r (strictly, for a low degree of curvature of the planar surface). When the surface is curved, the limit of applicability of these equations is reached earlier than the limit of applicability of thermodynamics in general, so that the limit of applicability of Eqns. (26)–(28) must be determined not from general molecular considerations but from an analysis of the equations themselves and the assumptions on which their derivation is based.

In the second place, the quantity r in Eqns. (26)–(28) characterises not the actual dimensions of the new phase but the dimensions of a geometric figure bounded on all sides by a surface of tension. At high values of r, the difference between the positions of the physical and geometric surfaces is negligibly small, since the surface of tension lies inside the surface layer. At small values of r, comparable with the thickness of the surface layer, this difference becomes appreciable and cannot be neglected. At the moment when the surface of tension disappears ($r = 0$), there still exists a microheterogeneity corresponding to a definite molecular complex. Thus the condition $r = 0$ is quite conceivable and physically real, so that rigorous thermodynamic equations should include this limiting case.

Rigorous thermodynamic analysis of curved surfaces[30] shows that for precise equations describing the dependence of the parameters of thermodynamic equilibrium on the curvature of the surface, two limiting cases can be considered: for large and small values of r. In the first case ($r \to \infty$) the precise thermodynamic equations become the Kelvin, Thomson, and Ostwald–Freundlich relationships, and in the second case ($r \to 0$) they acquire a different form.

Let us consider as an example the differential thermodynamic equation[30] describing the change in the vapour pressure for drops having very small dimensions:

$$\left(\frac{dp^{(2)}}{dr}\right)_T \simeq -\frac{\sigma A}{m^{(A)} r \left(v^{(2)} - v^{(A)}\right)}, \qquad (29)$$

where $m^{(A)}$ and $v^{(A)}$ are the mass and molar volumes of the surface layer, $v^{(2)}$ is the molar volume of the vapour, and $A = 4\pi r^2$. The surface tension approaches zero proportionately with the radius of curvature[30], so that with decrease in r the numerator of the right-hand side of (29) approaches zero as a quantity of the third order of smallness. Since the mass of the surface layer at the moment when the surface of tension disappears is not yet zero, the denominator of the right-hand side of (29) approaches zero as a quantity of the first order of smallness. Thus from (29) we have

$$\lim_{r \to 0} \left(\frac{dp^{(2)}}{dr}\right)_T = 0. \qquad (30)$$

The same result is obtained if we assume that the surface tension is constant and equal to its value at the boundary of the macro-phases.

Condition (30) implies that the state where r becomes zero corresponds to a finite limiting supersaturation P_0/P_∞ (Fig. 2), and this agrees completely with experiment and with the thermodynamic theory of the boundary of stability. It can be seen from Fig. 2 that the increase in vapour pressure with decrease in the radius of curvature is described satisfactorily by Kelvin's equation up to a certain limit, after which the curves corresponding to Kelvin's equation and the precise thermodynamic equation diverge sharply. This takes place when the quantity r becomes commensurate with the thickness of the surface layer.

An interesting feature is that the dimensions of the physical heterogeneity at the moment when the surface of tension disappears ($r = 0$) are also close to the thickness of the surface layer, so that the calculations of the size of the minimal nucleus, carried out from Kelvin's formula[56,63], may sometimes give a result close to the true value. In actual fact, use of the value of the limiting supersaturation P_0/P_∞ and Kelvin's equation gives the radius r_0 (Fig. 2). If this radius is close to the limit where the continuous and broken curves in Fig. 2 diverge (in other words, if the continuous curve approximates sufficiently accurately to the broken curve when $r > r_0$ and to the horizontal line when $r < r_0$), r_0 is close to the thickness of the surface layer and hence close to the dimensions of the microheterogeneity corresponding to the condition $r = 0$. We cannot, however, be sure that the value of r_0 calculated from Eqns. (26)–(28) will always give a correct value for the minimal critical dimensions of the nucleus, for when this occurs a correct result will be due to "mutual cancellation" of two errors: the assumption that Eqns. (26)–(28) are applicable in the range of small values of r and the assumption that the quantity r coincides with the dimensions of the physical heterogeneity.

Since the surface of tension disappears with retention of the microheterogeneity, it is of interest to examine the result obtained using another geometric surface, which was also derived by Gibbs and corresponds to the case where the surface excess Γ of a substance in a one-component system becomes zero. This surface exists so long as the smallest heterogeneity is present[30].

Using the symbols σ' and r' to denote the surface tension and radius of curvature corresponding to the surface $\Gamma = 0$, we can write an expression for the work of formation of an equilibrium nucleus as follows[20,21]:

$$W = \frac{4}{3}\pi (r')^2 \left(\sigma' - r' \frac{d\sigma'}{dr'}\right). \qquad (31)$$

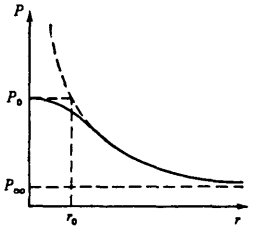

Fig. 2. Dependence of the equilibrium vapour pressure on the radius of curvature of the surface of tension according to Kelvin's equation and the precise thermodynamic equation.

From expression (31) it was concluded[64,65] that zero work of formation of a nucleus corresponds to the condition

$$\frac{\sigma'}{r'} = \frac{d\sigma'}{dr'}, \qquad (32)$$

and to a nucleus of finite dimensions. This conclusion was contrasted[65] with Gibbs' theory, which leads to formula (14). If, however, we bear in mind the difference between the geometric surfaces used in the derivation of relationships (31) and (14), it can readily be seen that the latter are quite adequate. The quantity σ' should in actual fact satisfy Kondo's equation

$$\sigma' = \frac{\sigma r^2}{3(r')^2} + \frac{1}{3} r' (P^{(1)} - P^{(2)}), \qquad (33)$$

where the quantities without primes, as before, relate to the surface of tension. From (33) we obtain

$$\frac{\sigma'}{r'} - \frac{d\sigma'}{dr'} = \frac{\sigma r^2}{(r')^3} > 0, \qquad (34)$$

from which it follows that condition (32) cannot be satisfied at finite values of r and is observed only when $r = 0$, in complete agreement with Gibbs' theory. Finally, substitution of (34) in (31) leads to the Gibbs formula (14).

Thus the work of formation of an equilibrium nucleus is found to be independent of the choice of geometric surface and equal, under the conditions considered, to one-third of the product of the area of the surface of tension and its surface tension. The fact that the work of formation of a nucleus becomes equal to zero when the surface of tension, and not any other surface, disappears, emphasises once again the physical significance of this important concept.

We have still to determine whether the use of the surface $\Gamma = 0$ is necessary in the range of small values of r', when the surface of tension no longer exists. Formally, the surface $\Gamma = 0$ can be found for molecular aggregates of any degree of smallness: even dimers, in which the distances between the molecules are less than the average distance between the molecules in a large mass, should exhibit definite "surface excesses" of substance. The use of these concepts in the range of very small values of r' is questionable, however. In addition to the fact that the thermodynamic method is here crossing the boundary of its applicability, we are also faced with the question of whether these systems can be regarded as heterogeneous. Any homogeneous phase is characterised by the presence of a whole series of molecular complexes in equilibrium with one another (monomers, dimers, trimers, etc.) and it is generally assumed[35,59] that there exists a definite minimal dimension for a new formation, at which it can be regarded as a deviation from homogeneity. If we define this minimal dimension as that corresponding to the disappearance of the surface of tension, it becomes unnecessary to consider the formation of new phases beyond the limit of existence of the surface of tension.

From all that has been said in the present Section, it follows that the limiting supersaturation is finite and corresponds to the state where the radius of curvature of the surface of tension becomes zero; the use of the surface of tension in the thermodynamics of microheterogeneous systems makes it possible to combine the theories of macro- and micro-heterogeneous equilibria into a single logical system and to define clearly the boundary between homogeneous and heterogeneous states.

7. THE FORMATION OF A NEW PHASE UNDER ISOCHORIC-ISOTHERMAL CONDITIONS

The isobaric-isothermal process conditions examined above assume that the formation of a new phase does not lead to a change in the mechanical state of the surrounding medium, although it may be accompanied by a change in composition. In practice this means that the whole system is under a constant external pressure (for example, atmospheric) and that the rate of attainment of mechanical equilibrium between the external part of the system and the immediate surroundings of the nucleus is very much greater than the rate of formation of the nucleus. These two conditions are not always satisfied. As pointed out by Frenkel'[35], the formation of a nucleus of liquid in a crystal may be accompanied by an increase in pressure and deformation of the crystal in the region adjoining the nucleus. The condensation of vapour in a closed vessel is also accompanied by a change in pressure.

In order to allow for the change in the mechanical state of the medium when a new phase is formed, we shall assume, as before, that the process takes place isothermally, but we shall replace the constant-pressure condition by the constant-volume condition. The work of formation of a new phase under isochoric-isothermal conditions is found from (11) as the difference in the free energies of the final and initial states of the process. For the initial state we have

$$F_{\text{hom}} = -PV + \sum_i \mu_i m_i \qquad (35)$$

and for the final state

$$F_{\text{het}} = -P^{(1)}V^{(1)} - P^{(2)}V^{(2)} + \sigma A + \sum_i \mu_i^{(1)} m_i^{(1)} + \sum_i \mu_i^{(2)} m_i^{(2)}, \qquad (36)$$

where $V^{(1)} + V^{(2)} = V$ and $m_i^{(1)} + m_i^{(2)} = m_i$.

Thus

$$\Delta F = F_{\text{het}} - F_{\text{hom}} = (P^{(2)} - P^{(1)})V^{(1)} + (P - P^{(2)})V + \sigma A + \sum_i (\mu_i^{(1)} - \mu_i^{(2)}) m_i^{(1)} + \sum_i (\mu_i^{(2)} - \mu_i) m_i. \qquad (37)$$

It is interesting to compare the work of the isobaric-isothermal and isochoric-isothermal processes leading to the same final state. From (21) and (37) we have

$$\Delta\Phi - \Delta F = -(P - P^{(2)})V + \sum_i \left[\mu_i(P) - \mu_i(P^{(2)})\right] m_i. \qquad (38)$$

If we make use of the expansion

$$\mu_i(P^{(2)}) = \mu_i(P) + v_i(P^{(2)} - P) + \frac{1}{2}\frac{\partial v_i}{\partial P}(P^{(2)} - P)^2 + \ldots, \qquad (39)$$

where v_i is the partial molar volume of the i-th component, we can writen (38) in the form

$$\Delta\Phi - \Delta F \simeq -\frac{1}{2}\left(\frac{\partial V}{\partial P}\right)_T (P^{(2)} - P)^2 > 0, \qquad (40)$$

from which it follows that $\Delta\Phi > \Delta F$, irrespective of the sign of the difference $P^{(2)} - P$. Thus allowance for the change in the mechanical state of the medium during the formation of a nucleus of the new phase leads to a decrease in the work of formation of a nucleus of given dimensions.

By differentiating (37), taking account of the fundamental equation for the nucleus (4), we can readily show that the condition for equilibrium between the medium and the nucleus corresponds to an extremal value of ΔF:

$$\Delta F_0 = \frac{1}{3}\sigma A + (P - P^{(2)})V + \sum_i (\mu_i^{(2)} - \mu_i) m_i. \qquad (41)$$

The nature of the extremum is determined by the sign of the second differential

$$(d^2\Delta F)_0 = -8\pi\sigma\,(dr)^2 + \left[d\sigma\,dA - dP^{(1)}\,dV^{(1)} + \sum_i d\mu_i^{(1)} dm_i^{(1)}\right] + \left[-dP^{(2)}\,dV^{(2)} + \sum_i d\mu_i^{(2)}\,dm_i^{(2)}\right]. \quad (42)$$

As in the case of isobaric-isothermal conditions, the expression for the second differential of the work of formation of the new phase contains, in addition to the first term, which is clearly negative, two positive terms in square brackets. The first of these characterises the internal stability of the nucleus and the second the internal stability of the medium (metastable phase). The magnitude of the second term in the square brackets is higher, the greater the changes in the state of the medium as a result of growth of the new phase. Under certain conditions, therefore, expression (42) as a whole may become positive and the quantity (41) will correspond not to a maximum but to a minimum of ΔF (that this is in fact the case will be demonstrated in the next Section for the case of the condensation of a vapour). However, if the growth of the nucleus is accompanied by a small change in the state of the medium, expression (42) is negative and (41) corresponds to the maximal work.

Unlike Eqn. (23), expression (41) does not become the Gibbs formula (14), even for one-component systems. It cannot therefore be concluded on the basis of expression (41) that the work of formation of the equilibrium nucleus is always positive and always increases with increase in its dimensions. Only for very large systems, when the change in pressure and chemical potentials can be neglected, does expression (41) approximate to the Gibbs formula (14).

Thus examination of the isochoric-isothermal conditions for a phase change in the general form shows that this case exhibits a number of unique features. For greater clarity we shall reexamine these in the next Section for the case of the condensation of a single-component gas.

8. THE ISOCHORIC-ISOTHERMAL CONDENSATION OF A VAPOUR

One of the characteristic features of an isochoric-isothermal process is that all the substance necessary for the formation of a heterogeneous system of a given volume is from the very beginning concentrated in this volume in the form of a homogeneous mass (in the case of the isobaric process the substance enters the given volume as formation of the new phase proceeds). Thus the initial state of the system may correspond to such a marked degree of supersaturation that it will lie not in the metastable but in the unstable range. It is clear that the use of the ideal-gas and ideal-solution equations in this case is impossible in principle, since these equations relate to stable phases. The final state of the system always corresponds to a metastable state of the medium and is not necessarily characterised by high supersaturation. The use of the ideal-gas and ideal-solution equations here becomes possible in principle, and we can consider merely the corrections, if these are sufficiently large.

To take a specific example, let us consider the isochoric-isothermal condensation of a vapour and estimate firstly the magnitude of the third term in (42), which characterises the stability of the final (metastable) state of the vapour in equilibrium with drops of liquid. In the solution of this problem we can assume that the vapour is ideal.

For a one-component ideal gas, this term is equal to

$$-dP^{(2)}\,dV^{(2)} + d\mu^{(2)}\,dm^{(2)} = m^{(2)}RT\,(d\ln P^{(2)})^2 = m^{(2)}RT\left(\frac{d\ln P^{(2)}}{dr}\right)^2 (dr)^2, \quad (43)$$

and its relative role in (42) depends on the way in which the coefficient preceding $(dr)^2$ changes with growth of the new phase. Using the relationships $P^{(2)} = m^{(2)}RT/V^{(2)}$, $m = m^{(1)} + m^{(2)}$, and $V = V^{(1)} + V^{(2)}$, we obtain

$$m^{(2)}RT\left(\frac{d\ln P^{(2)}}{dr}\right)^2 = m^{(2)}RT\left(\frac{4\pi r^2}{V^{(2)}} - \frac{1}{m^{(2)}}\frac{dm^{(1)}}{dr}\right)^2. \quad (44)$$

The value of r cannot exceed a certain maximal possible value r_{max} corresponding to total conversion of the material into the liquid state. It is evident that as $r \to r_{max}$, $m^{(2)}$ approaches zero and the coefficient preceding $(dr)^2$ increases without limit. If the dimensions of the new phase are sufficiently large, this coefficient becomes greater than $8\pi\sigma$ and stable equilibrium will be observed.

The change from unstable to stable equilibrium between the drop and vapour should be accompanied by a decrease in the work of its formation and hence the curve giving the dependence of ΔF_0 on r should show a maximal value of ΔF_0 which is positive (Fig. 3). The curve in Fig. 3 should not be confused with the usual curves giving the dependence of the work of formation of a non-equilibrium nucleus on its size, where the maximum corresponds to the formation of an equilibrium nucleus: in this case only equilibrium quantities are plotted on the axes.

The form of the dependence of ΔF_0 on r (Fig. 3) can readily be explained by a graphical method. To determine the points on the graph corresponding to equilibrium between the drop and the vapour, two relationships must be known: (1) the dependence of the equilibrium vapour pressure on the drop size (this relationship is shown in Fig. 2) and (2) the dependence of the vapour pressure on the drop size in a given system with mechanical transfer of substance from the vapour to the liquid. The second relationship is not concerned with the equilibrium but is related to the fact that since the total volume of the system and the difference between the densities of the phases are constant, the change in the volume $V^{(2)}$ associated with the vapour and the change in the mass of the vapour $m^{(2)}$ with growth of the liquid phase occur at different rates.

Let us assume that the gas obeys the van der Waals' equation and occupies a certain volume V. As the gas is converted into liquid its pressure P will change as follows:

$$\frac{dP^{(2)}}{dr} = \left[-\frac{RT}{(v^{(2)}-b)^2} + \frac{2a}{(v^{(2)})^3}\right]\frac{dv^{(2)}}{dr}, \quad (45)$$

where the molar volume of the vapour $v^{(2)} \equiv V^{(2)}/m^{(2)} = (V - V^{(1)})/(m - m^{(1)})$ also depends on the value of r:

$$\frac{dv^{(2)}}{dr} = -\frac{4\pi r^2}{m^{(2)}} - \frac{V^{(2)}}{(m^{(2)})^2}\frac{dm^{(1)}}{dr}. \quad (46)$$

To establish the shape of the $P^{(2)}(r)$ curve, it is sufficient to consider two limiting cases. In the first, when

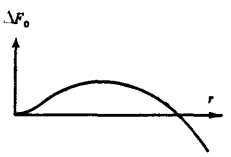

Fig. 3. Influence of the equilibrium dimensions of the new phase on the work of the isochoric-isothermal process.

$r \to 0$, the right-hand side of (46), and with it the right-hand side of (45), approach zero. At the same time $P^{(2)}$ becomes equal to the initial pressure P. The other limiting case corresponds to complete conversion of vapour into liquid, when $m^{(1)}$, $V^{(1)}$, and r reach their maximal values, and $m^{(2)}$ and $P^{(2)}$ become zero. In this case $v^{(2)}$ and the right-hand side of (46) increase without limit, but the right-hand side of (45) remains a finite negative quantity. From this it follows that the curve describing the change in pressure when the substance is converted from vapour into liquid should be concave towards the r axis (Fig. 4). The limiting slope α of this curve is greater, the higher the initial pressure P.

With the curves given in Figs. 2 and 4 we can consider all possible cases of equilibrium, since they are defined on the graph giving the dependence of $P^{(2)}$ on r by the points of intersection of these curves. Fig. 5 gives examples of their mutual disposition.

The case a ($P \leq P_\infty$) corresponds to unsaturated or, in the limit, saturated vapour. The curves do not intersect and equilibrium (if the liquid is conceived as a spherical drop) is impossible.

The case c ($P_0 > P > P_\infty$) corresponds to initial supersaturation of the vapour within the limits of the metastable range. Since the curve in Fig. 2 for a great part of its length is concave, and the curve in Fig. 4 convex towards the r axis, they must intersect in two points (A and B). It can readily be seen that one of these points (point A) corresponds to unstable equilibrium and the other (point B) to stable equilibrium. In actual fact, if it is assumed that the radius of a drop existing initially in state A increased accidentally, the equilibrium vapour pressure of the drop, in accordance with Fig. 5, curve c, will be less than the pressure in the surrounding medium and the drop will continue to grow. On the other hand, with an accidental decrease in the dimensions of the drop, its equilibrium pressure increases to a greater extent than the pressure in the surrounding medium and the drop will volatilise — the equilibrium is unstable. At the point B on the other hand, an accidental change in the dimensions of the drop leads to a ratio between the equilibrium vapour pressure and the pressure in the surrounding medium which restores the drop to its original dimensions — the equilibrium is completely stable.

Thus a given value of P corresponds not to one but to two equilibrium states: the first of these is unstable and corresponds to the Gibbs–Volmer nuclei, while the second is stable and corresponds to particles of large dimensions.

An intermediate case between a and c is case b, where the curves merely touch. The equilibrium corresponding to this case is stable with respect to condensation and unstable with respect to volatilisation. An interesting feature is that on going from a to c the dimensions of the Gibbs–Volmer nuclei and the stable new formations may be as close to one another as desired. Case b corresponds to the maximal work of formation of the equilibrium nucleus (maximum in Fig. 3). With increase in the initial supersaturation, the work of formation of both the unstable and stable drops decreases.

Case e in Fig. 5 corresponds to a high initial supersaturation, which brings the vapour into an unstable state. The curves intersect only once, corresponding to the formation of a fairly large stable drop. When the initial state becomes unstable, the shape of the initial section (at small values of r) of the curve in Fig. 4 may change in such a way that a maximum value of $P^{(2)}$ is produced. This cannot, however, influence the conclusion that the final state is unique and stable. The work of formation of a new phase in case e is negative and the process of phase change takes place at a high rate.

An intermediate case between c and e is case d, where the initial supersaturation of the vapour corresponds to the boundary of stability relative to continuous changes. In case d the dimensions of the unstable equilibrium nucleus and its work of formation are equal to zero.

This examination confirms the relationships shown in Fig. 3. To make the picture of the change in ΔF during the formation of a new phase more complete, we have given curves (Fig. 6) describing the formation of non-equilibrium nuclei and larger drops for different initial conditions (for cases a, b, c, d, and e examined above). The extremal points on these curves correspond to equilibrium states.

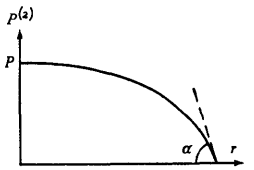

Fig. 4. Change in vapour pressure as the substance is converted from the vapour into the condensed phase under isochoric conditions.

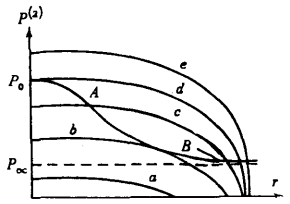

Fig. 5. Possible cases of equilibrium for the isochoric-isothermal condensation of vapour.

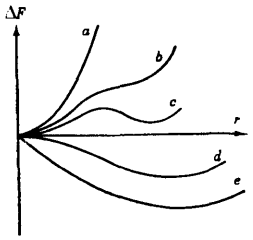

Fig. 6. Change in ΔF with change in the dimensions of the new phase for different initial supersaturations.

From Fig. 6, as from Fig. 3, it can be seen that in a certain range of dimensions the formation of stable drops takes place with expenditure of work (as does the formation of unstable equilibrium nuclei) so that the state of these drops is metastable with respect to the initial state. The probability of volatilisation of these drops is still fairly high. True stable states will correspond to greater supersaturation, which need not reach the boundaries of stability of the vapour.

The qualitative examination carried out in the present section can readily be extended to subliming crystals, by taking account of relationships (5) and (6). Since the shape of the solubility curve is the same as that of the curve in Fig. 2, an analogous discussion can be extended to the processes of crystallisation from solutions.

9. THE FORMATION OF A NEW PHASE UNDER ISOBARIC-ISENTROPIC CONDITIONS

Up to the present, in accordance with the general pattern, we have assumed that the process of new-phase formation is isothermal. In other words, we have assumed that the whole system is immersed in a thermostat at constant temperature and that the rates of attainment of thermal equilibrium between the system and thermostat, and between the nucleus and the medium, are very much greater than the rate of formation of the new phase. It cannot be assumed that these conditions are always satisfied[66] and it is necessary to discuss the changes in the thermodynamic formulae, introduced by departure from these conditions in finite systems.

If the system is thermally isolated, the process of new-phase formation will take place adiabatically. Thermodynamically, however, it is more convenient to deal with the isentropic process, since this makes it possible to use expressions (9) and (10) to calculate the work of formation of the new phase. The two types of process coincide only for reversible changes and the assumption that the entropy is constant generally assumes some heat exchange between the system and external bodies. It is possible that this assumption corresponds more closely to actual conditions than the assumption that thermal isolation is complete.

Let us assume in the present section that the formation of a new phase takes place at constant total entropy of the system S and external pressure $P^{(2)}$. The work of formation of the new phase under these conditions is found from formula (10). For the initial state we have

$$H_{\text{hom}} = TS + \sum_i \mu_i m_i, \tag{47}$$

and for the final state

$$H_{\text{het}} = T^{(1)} S^{(1)} + T^{(2)} S^{(2)} + (P^{(2)} - P^{(1)}) V^{(1)} + \sigma A + \sum_i \mu_i^{(1)} m_i^{(1)} + \sum_i \mu_i^{(2)} m_i^{(2)}, \tag{48}$$

where T is the initial temperature of the system and $T^{(1)}$, $S^{(1)}$ and $T^{(2)}$, $S^{(2)}$ are the final temperatures and entropies of the nucleus and medium respectively.

Subtracting (47) from (48) and making allowance for the fact that the total entropy and masses of the components are constant, we obtain

$$\Delta H = (T^{(1)} - T^{(2)}) S^{(1)} + (T^{(2)} - T) S + (P^{(2)} - P^{(1)}) V^{(1)} + \sigma A + \sum_i (\mu_i^{(1)} - \mu_i^{(2)}) m_i^{(1)} + \sum_i (\mu_i^{(2)} - \mu_i) m_i. \tag{49}$$

Expression (49) gives the work of formation of a new phase with volume $V^{(1)}$, component masses $m_i^{(1)}$, and entropy $S^{(1)}$ for an isobaric-isentropic process. It can readily be shown that the first differential of this expression becomes zero when equilibrium conditions are reached, namely, equality of temperatures and chemical potentials and fulfilment of condition (3). Substituting the same conditions in (49), we find the extremal value of the work of formation of the new phase:

$$\Delta H_0 = \frac{1}{3} \sigma A + (T^{(2)} - T) S + \sum_i (\mu_i^{(2)} - \mu_i) m_i. \tag{50}$$

This relationship differs from the Gibbs relationship (14) in that it contains additional terms which take account of the change in the thermal and chemical states of the system during the formation of the new phase. For a very large system these terms are small and the two relationships almost coincide.

It is of interest to compare the work of formation of an equilibrium nucleus of given dimensions, carried out isentropically with change in the temperature of the system from T to $T^{(2)}$, with the corresponding quantity for the isothermal process at temperature $T^{(2)}$. From (50) and (23) we have

$$\Delta\Phi_0 - \Delta H_0 = -(T^{(2)} - T) S - \sum_i \left[\mu_i (T^{(2)}) - \mu_i (T)\right] m_i. \tag{51}$$

By making use of the expansion

$$\mu_i (T^{(2)}) = \mu_i (T) - s_i (T^{(2)} - T) - \frac{1}{2} \frac{\partial s_i}{\partial T} (T^{(2)} - T)^2 - \dots, \tag{52}$$

where s_i is the partial molar entropy of the i-th component in the initial state of the system, we can write (51) in the following approximate form:

$$\Delta\Phi_0 - \Delta H_0 \simeq \frac{1}{2} \left(\frac{\partial S}{\partial T}\right)_P (T^{(2)} - T)^2 > 0. \tag{53}$$

It follows from expression (53) that the correction for non-isothermal character in the process, like the correction for non-isobaric character, leads to a decrease in the magnitude of the work of formation of an equilibrium nucleus of given dimensions.

To study the nature of the extremal value of ΔH, corresponding to the equilibrium state of the new phase, we use Eqn. (4) and the equilibrium condition to find the second differential of ΔH:

$$(d^2 \Delta H)_0 = -8\pi\sigma (dr)^2 + \left[dT^{(1)} dS^{(1)} - dP^{(1)} dV^{(1)} + d\sigma\, dA + \sum_i d\mu_i^{(1)} dm_i^{(1)}\right] + \left[dT^{(2)} dS^{(2)} + \sum_i d\mu_i^{(2)} dm_i^{(2)}\right]. \tag{54}$$

This relationship differs from the analogous relationships (24) and (42) in that it contains additions terms $dT^{(1)} dS^{(1)}$ and $dT^{(2)} dS^{(2)}$ which take account of the possibility of change in the thermal state of the nucleus and medium. The term $dP^{(2)} dV^{(2)}$, as in the case of (24), does not appear, since the pressure $P^{(2)}$ is assumed to be constant. We have represented the right-hand side of (54) in the form of three terms, the first of which is clearly negative, while the other two in the square brackets are positive for stable states. The first of the terms in the square brackets characterises the internal stability of the nucleus of the new phase and the second the internal stability of the metastable phase. For the case where growth of the nucleus is not reflected in the state of the medium, the second term is equal to zero — like the additional terms on the right-hand side of (50) — and there is a maximum value of ΔH for the formation of the equilibrium nucleus, in complete

accordance with Volmer's theory. If, however, growth of the nucleus is accompanied by a marked change in the state of the medium, the second term may acquire sufficiently high positive values to make the whole of the right-hand side of (54) positive. This corresponds to stable equilibrium between the new phase and the medium, characterised by a minimum value of ΔH.

To illustrate this possibility, let us estimate the magnitude of the last term for an ideal gas. Using the expressions for the entropy and chemical potential of an ideal gas (assumed to be monatomic)

$$S^{(2)} = \frac{5}{2} m^{(2)} R \ln T^{(2)} + m^{(2)} f(P^{(2)}), \quad (55)$$

$$\mu^{(2)} = \frac{5}{2} RT^{(2)} - \frac{5}{2} RT^{(2)} \ln T^{(2)} - T^{(2)} f(P^{(2)}), \quad (56)$$

we obtain

$$dT^{(2)} dS^{(2)} + d\mu^{(2)} dm^{(2)} = \frac{5}{2} m^{(2)} RT^{(2)} (d \ln T^{(2)})^2 = \frac{5}{2} m^{(2)} RT^{(2)} \left(\frac{d \ln T^{(2)}}{dr}\right)^2 (dr)^2. \quad (57)$$

Using the equation of state for an ideal gas $m^{(2)} RT^{(2)} = P^{(2)} V^{(2)}$ and the condition that the mass of the system $m_i = m^{(1)} + m^{(2)}$ is constant, we can express the result obtained in the form

$$\frac{5}{2} m^{(2)} RT^{(2)} \left(\frac{d \ln T^{(2)}}{dr}\right)^2 = \frac{5}{2} m^{(2)} RT^{(2)} \left(\frac{d \ln V^{(2)}}{dr} + \frac{1}{m^{(2)}} \frac{dm^{(1)}}{dr}\right)^2. \quad (58)$$

The derivative $d \ln V^{(2)}/dr$ cannot be expressed in explicit form as was previously done for the derivative $d \ln P^{(2)}/dr$ in formula (44), since the total volume of the system in this case is variable. From expression (58), as from expression (44), however, it follows that the magnitude of the whole expression increases without limit with decrease in $m^{(2)}$. This result is physically understandable, since with a relative increase in the mass of the new phase its influence on the state of the medium will continue to increase. When the new-phase range reaches definite dimensions, the magnitude of (58) exceeds $8\pi\sigma$ and the equilibrium becomes stable.

Thus examination of isobaric-isentropic processes reveals qualitatively the same regular features as in the case of isochoric-isothermal conditions: the work of formation of a new phase becomes less than the work under isobaric-isothermal conditions; with increase in the equilibrium dimensions of the new phase, the work of its formation ΔH_0 at first increases and then decreases, entering the range of negative values; relatively small ranges of new phase (nuclei) correspond to unstable equilibria with the medium, whereas relatively large ranges correspond to stable equilibrium.

10. THE FORMATION OF A NEW PHASE UNDER ISOCHORIC-ISENTROPIC CONDITIONS

Abandoning conditions of constant temperature and pressure, let us assume that the process of new-phase formation takes place under isochoric-isentropic conditions. This is the most general of all the cases considered, since it assumes a change in the chemical, thermal, and mechanical state of the system during the formation and growth of the new phase.

The work of formation of a new phase under isochoric-isentropic conditions is found from formula (9). For the initial homogeneous state of the system we have

$$U_{\text{hom}} = TS - PV + \sum_i \mu_i m_i. \quad (59)$$

and for the final heterogeneous state

$$U_{\text{het}} = T^{(1)} S^{(1)} + T^{(2)} S^{(2)} - P^{(1)} V^{(1)} - P^{(2)} V^{(2)} + \sigma A + \sum_i \mu_i^{(1)} m_i^{(1)} + \sum_i \mu_i^{(2)} m_i^{(2)}. \quad (60)$$

Taking account of the fact that the total entropy, total volume, and component masses are constant, we obtain from (60) and (59) an expression for the work of formation of the new phase

$$\Delta U = (T^{(1)} - T^{(2)}) S^{(1)} + (T^{(2)} - T) S + (P^{(2)} - P^{(1)}) V^{(1)} + (P - P^{(2)}) V + \sigma A + \sum_i (\mu_i^{(1)} - \mu_i^{(2)}) m_i^{(1)} + \sum_i (\mu_i^{(2)} - \mu_i) m_i. \quad (61)$$

For the equilibrium state of the heterogeneous system

$$\Delta U_0 = \frac{1}{3} \sigma A + (T^{(2)} - T) S + (P - P^{(2)}) V + \sum (\mu_i^{(2)} - \mu_i) m_i. \quad (62)$$

This result differs from the Gibbs formula (14) in that it contains additional terms which take account of the change in the thermal, mechanical, and chemical state of the system during the formation of the new phase. For an infinitely large system these terms are equal to zero and (62) becomes (14).

Allowance for the changes in the thermal and mechanical states of the system during the formation of the new phase was made separately in sections 9 and 7, and we saw that these two changes act in the same direction, decreasing the work of formation of the new phase with increase in its dimensions. We can therefore be sure that a simultaneous change in the thermal and mechanical state of the system will have an influence in the same direction, so that the dependence of ΔU_0 on the dimensions of the new phase will be characterised by the same qualitative relationships as the dependence of ΔF_0 and ΔH_0 on these dimensions. Moreover, the simultaneous action of factors decreasing the work of formation of the new phase will apparently cause the quantity ΔU_0 to be smaller than the corresponding quantities $\Delta \Phi_0$, ΔF_0, and ΔH_0.

11. THE HETEROGENEOUS FORMATION OF NEW PHASES

In examining the influence of the imposed conditions on the work of formation of a new phase, we have until now assumed that the formation of the new phase is brought about by a homogeneous mechanism. Let us now consider the heterogeneous mechanism.

Gibbs[13] obtained the following expression for the work of formation of an equilibrium lenticular mass (*1*) at the planar boundary between two infinitely-extended phases (*2*) and (*3*) (Fig. 7):

$$W = \frac{1}{3} (\sigma_{12} A_{12} + \sigma_{13} A_{13} - \sigma_{23} A_{23}), \quad (63)$$

where σ_{12}, σ_{13}, and σ_{23} are the surface tensions at the boundaries between the first and second, first and third,

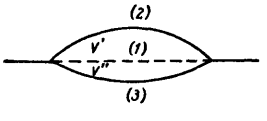

Fig. 7. Formation of a lenticular mass at a planar boundary between two phases.

and second and third phases respectively, A_{12} and A_{13} the areas of contact between the lens and the second and third phases respectively, and A_{23} is that part of the area of contact between the second and third phases which disappears when the lens is formed (broken line in Fig. 7). Gibbs' expression (63) is a generalisation of his formula (14) for the case of a heterogeneous process. This expression can be written in the slightly different form

$$W = \frac{\sigma_{12} V'}{r_{12}} + \frac{\sigma_{13} V''}{r_{13}}. \qquad (64)$$

where V' and V'' are the volumes of the second and third phases replaced by the new phase ($V' + V'' = V^{(1)}$), and r_{12} and r_{13} the radii of curvature of the surfaces of the lenticular mass.

If the formation of the new phase takes place on the planar surface of a solid (Fig. 8), the second term on the right-hand side of (64) disappears and the magnitude of the work will be determined by the relationship

$$W = \frac{\sigma_{12} V^{(1)}}{r_{12}}. \qquad (65)$$

It can readily be seen that formula (14) can be brought to exactly the same form, and we can equate directly the work of the heterogeneous process and the work of the homogeneous process, both for a given radius of curvature of the nucleus and for a given nucleus volume. For nuclei with identical radii of curvature (the surface tensions in this case will also be identical) with a contact angle of wetting $\theta < 180°$, the volume of the heterogeneous nucleus amounts to only a fraction of the volume of the homogeneous nucleus and hence the work of the heterogeneous process will be less than that of the homogeneous process. In the comparison of nuclei of equal volume, allowance must be made for the change in the surface tension with the radius of curvature of the surface. If it is assumed that at small values of r the surface tension depends linearly on r,[30] there is no difference between the work of the heterogeneous process and that of the homogeneous process in the range of small values of r and large values of θ. Since for equal volumes a heterogeneous nucleus has small curvature, however, the heterogeneous process will correspond to a lower supersaturation. With increase in the wettability of the surface of the solid, the work of the heterogeneous formation of the nucleus decreases, and at values of θ close to zero it is necessary to take account of the perimeter energy of the now almost two-dimensional nucleus.

For given values of the wetting angle θ and the curvature of the nucleus at its boundary with the liquid or gaseous phase, the change from a planar to a convex solid surface corresponds to an increase in the volume of the nucleus; the change from a planar to a concave surface corresponds to a decrease in the volume of the nucleus (Fig. 8). On the basis of expression (65) (although the latter is not now rigorous), it may be concluded that the change from a planar to a convex surface leads to an increase, and the change from a planar to a concave surface to a decrease, in the work of the heterogeneous formation of the new phase.

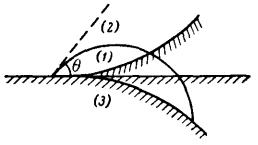

Fig. 8. Formation of a new phase on the surface of a solid.

A particular case is the heterogeneous formation of an equilibrium nucleus in the form of a closed layer on a condensation or crystallisation nucleus. The magnitude of the work of this process is given by the expression

$$W = \sigma_{12}\left(A_{12} - A_{13}\cos\theta - \frac{2V^{(1)}}{r_{12}}\right). \qquad (66)$$

If the equilibrium nucleus and the condensation or crystallisation nucleus are spherical, this expression becomes Krystanov's formula[67,68]:

$$W = \frac{1}{3}\sigma_{12} A_{12}\left[1 - 3\left(\frac{r_{13}}{r_{12}}\right)^2 \cos\theta + 2\left(\frac{r_{13}}{r_{12}}\right)^3\right]. \qquad (67)$$

Analysis of this formula shows[67] that in the range of wetting angles $0 \leqslant \theta \leqslant 48°12'$ the work of the heterogeneous formation of an equilibrium nucleus is always less than the work of the homogeneous process. In the range $48°12' < \theta < 90°$, there exists for each value of θ a critical magnitude of the condensation or crystallisation nucleus from which the work of the heterogeneous process exceeds the work of the homogeneous process. Finally, at $\theta \geqslant 90°$ the work of the heterogeneous formation of the nucleus is always greater than the work of the homogeneous process.

Formulae (63)–(65) are applicable for finite systems only if the process of new-phase formation takes place at constant pressure, temperature, and chemical potentials and hence at constant surface tension. These formulae make no allowance for change in the thermal, mechanical, and chemical state of the system during the formation of the new phase and assume that these changes are compensated by the action of external forces. This does not always correspond to real conditions and it is necessary to discuss the corrections which must be introduced into formula (63) when different process conditions are considered.

Let us assume that the production of a new phase at a plane interface takes place under isochoric-isentropic conditions. A characteristic feature of a heterogeneous process is that the initial and final states of the system are heterogeneous and both exhibit surface energy. For the initial equilibrium state we can write

$$U'_{het} = TS - PV + \sigma'_{23} A'_{23} + \sum_i \mu_i m_i, \qquad (68)$$

where σ'_{23} and A'_{23} are the surface tension and area of the interface in the initial state (Fig. 7). For the final state, which does not necessarily correspond to equilibrium between the new phase and the rest of the system, we have

$$U''_{het} = T^{(1)}S^{(1)} + T^{(2)}(S - S^{(1)}) - P^{(1)}V^{(1)} - P^{2}(V - V^{(1)}) + \\ + \sigma_{12}A_{12} + \sigma_{13}A_{13} + \sigma''_{23}A''_{23} + \sum_i \mu_i^{(1)} m_i^{(1)} + \sum_i \mu_i^{(2)}(m_i - m_i^{(1)}), \qquad (69)$$

where σ''_{23} and A''_{23} are the surface tension and area of the interface between the initial phases and the final state. By definition, $A_{23} = A'_{23} - A''_{23}$. Subtracting (68) from (69), we obtain

$$\Delta U = (T^{(1)} - T^{(2)})S^{(1)} + (T^{(2)} - T)S + (P^{(2)} - P^{(1)})V^{(1)} + (P - P^{(2)})V + \sigma_{12}A_{12} + \\ + \sigma_{13}A_{13} + \sigma''_{23}A''_{23} - \sigma'_{23}A'_{23} + \sum_i (\mu_i^{(1)} - \mu_i^{(2)}) m_i^{(1)} + \sum_i (\mu_i^{(2)} - \mu_i) m_i. \qquad (70)$$

Expression (70) gives the work of formation of a new phase at the boundary between the two phases under isochoric-isentropic conditions. Comparison with Eqn. (61)

shows that the corrections for the change in pressure, temperature, and chemical potentials in the system with the formation of the new phase are of the same form as in the case of the homogeneous process.

For the equilibrium state, expression (70) can be converted into the form

$$\Delta U_0 = \frac{1}{3}(\sigma_{12}A_{12} + \sigma_{13}A_{13} - \sigma''_{23}A_{23}) + (T^{(2)} - T)S + \\ + (P - P^{(2)})V + (\sigma''_{23} - \sigma'_{23})A'_{23} + \sum_i (\mu_i^{(2)} - \mu_i)m_i. \quad (71)$$

Relationship (71) exhibits two characteristics which distinguish it from the analogous relationship (62) for the work of the homogeneous formation of a new phase. Firstly, on going from (62) to (71), the first term becomes more complicated, but this does not change in physical significance; as before, it is one-third of the work of formation and disappearance of the interface. Secondly, on going from (62) to (71) we have an additional term $(\sigma''_{23} - \sigma'_{23})A'_{23}$ characterising the change in the state of the initial interface, which unavoidably accompanies the change in state of the coexisting phases during the formation of the nucleus. The magnitude of this additional term is small and can be neglected in comparison with the other corrections, except for the case where the volumes of the phases are relatively small (for example, when nuclei are formed in films).

Both characteristic features shown by relationship (71) should be preserved for other process conditions, and it is possible to write, without derivation,

$$\Delta H_0 = \frac{1}{3}(\sigma_{12}A_{12} + \sigma_{13}A_{13} - \sigma''_{23}A_{23}) + (T^{(2)} - T)S + (\sigma'_{23} - \sigma'_{23})A'_{23} + \\ + \sum_i (\mu_i^{(2)} - \mu_i)m_i, \quad (72)$$

$$\Delta F_0 = \frac{1}{3}(\sigma_{12}A_{12} + \sigma_{13}A_{13} - \sigma''_{23}A_{23}) + (P - P^{(2)})V + (\sigma''_{23} - \sigma'_{23})A'_{23} + \\ + \sum_i (\mu_i^{(2)} - \mu_i)m_i, \quad (73)$$

$$\Delta\Phi_0 = \frac{1}{3}(\sigma_{12}A_{12} + \sigma_{13}A_{13} - \sigma''_{23}A_{23}) + (\sigma''_{23} - \sigma'_{23})A'_{23} + \sum_i (\mu_i^{(2)} - \mu_i)m_i. \quad (74)$$

The corrections distinguishing relationships (71)–(74) from the Gibbs formula (63), with the exception of the correction (usually small) for surface tension, are the same as those for homogeneous processes. Thus the conclusions regarding the influence of process conditions on the magnitude of the work of formation of a new phase, reached for the case of homogeneous processes, remain completely applicable to heterogeneous processes and special analysis of expressions (71)–(74) is unnecessary.

---o0o---

It follows from the foregoing that the work of formation of new phases in real systems can be represented as the sum of two terms: the Gibbs work $W(r)$, determined by formula (14) or (63) depending on the mechanism of the process, and a correction $\Delta W(V)$, which depends on the dimensions of the system and the process conditions:

$$W = W(r) + \Delta W(V). \quad (75)$$

The introduction of the correction $\Delta W(V)$ makes it possible to follow not only the nucleation but also the growth of the new phase to macroscopic dimensions. This is convenient from the practical viewpoint, since it is then unnecessary to consider the dimensions of the nucleus to which a given formula is applicable. Analysis of relationship (75) leads to the conclusion that during growth, a bubble, drop, or crystallite of new phase passes first through a state of unstable equilibrium corresponding to the Gibbs–Volmer nuclei, after which, when sufficiently large dimensions are reached, it is converted into a state of stable equilibrium.

It should be noted that the conclusion regarding the stability of two-phase equilibrium under certain conditions is applicable for a system consisting of only two bodies, for example, a single drop and vapour. If it is assumed that two drops are present in the same volume, the result is altered significantly. In actual fact, if one of the drops volatilises with a decrease in its dimensions, it is found that although the vapour pressure in the system increases to a greater extent than the equilibrium vapour pressure of this drop (stable equilibrium condition), condensation takes place on the larger drop, leading finally to the disappearance of one of the drops. Thus the conclusion regarding the stability of the final state cannot be extended to systems consisting of many new-phase regions before these are converted into a single region, either by phase change (*via* vapour or solution) or by merging or collision. Nevertheless, this conclusion makes it possible to understand the reasons for the apparent stability of such systems; this stability, like that of polydisperse systems [69], is due to the low rate of attainment of equilibrium between the individual regions of new phase.

It is now of interest to discuss the part which may be played by the correction $\Delta W(V)$ strictly for the nuclei of the new phase. Usually the volume per nucleus in real systems is fairly large compared with the dimensions of the nucleus, and there is no doubt that Gibbs' assumption regarding the infinite nature of the system is applicable in this respect. Even if we make allowance for the change in surface tension for small radii of curvature and assume that $W(r)$ is a quantity not of the second but of the third order of smallness, the changes which may be produced by the formation of a nucleus in the fraction of the volume of the system corresponding to this nucleus lead only to a small correction $\Delta W(V)$.

These arguments, however, like the Gibbs theory, assume that in spite of the large magnitude of the system, equilibrium in it is established almost instantaneously, so that the whole system reacts with the nucleus formed. This is not always the case. In most cases the nucleus "succeeds" in reacting only with its immediate environment, so that the actual volume of the nucleus–medium system is much less than the volume per nucleus. The magnitude of the correction $\Delta W(V)$ in this case increases significantly.

The actual volume of the nucleus–medium system and the magnitude of the correction $\Delta W(V)$ depend on the rate of formation of the nucleus and the factors determining the rate of attainment of equilibrium, the coefficients of diffusion and self-diffusion, thermal conductivity, and the elastic properties of the medium. The relative part played by these factors differs for different processes. For example, the rate of diffusion plays an important part in condensation and crystallisation processes, particularly with mixtures. For processes involving fusion and the formation of drops of liquid in crystals, an important part is played by the mechanical factor associated with the deformation of the crystal in the region adjoining the drop. The correction $\Delta W(V)$ arising in this case may be fairly large and this possibly explains the almost complete absence of superheating in fusion processes.

Finally, one further important point should be noted. According to the above calculations, $\Delta W(V)$ is negative. In order to understand this result, it is necessary to remember that it is obtained by comparison of work values leading to the same final state. For infinite systems the initial and final supersaturations coincide. For finite systems the initial supersaturation is always greater than the final. Thus the formation of an equilibrium nucleus of given dimensions in a finite system requires a higher initial supersaturation than in the case of an infinite system, so that the process of new-phase formation in a finite system takes place more readily, with a lower expenditure of work.

If, however, we compare processes relating to the same initial state, the final states may correspond to a high activation energy, since for a given initial supersaturation the finite system corresponds to larger equilibrium-nucleus dimensions than does the infinite system. If the work of formation of a nucleus is calculated from the Gibbs formula for a given initial supersaturation, correction for the finite character of the system Q will give the expression

$$Q = W(r) + \Delta W(V) - W(r_0), \qquad (76)$$

where r_0 and r are determined from the equilibrium curve (for example, from the curve in Fig. 2) for the initial and final supersaturations respectively. For small values of $\Delta W(V)$, Q is always positive, since $r > r_0$.

Thus the thermodynamics of processes of new-phase formation leads to a kinetic equation having the form of (8), where Q involves not only diffusion but also the thermal conductivity and elastic properties of the medium.

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CHEMICAL PROPERTIES AND MOLECULAR STRUCTURE OF DERIVATIVES OF sym-HEPTAZINE[1,3,4,6,7,9,9b-HEPTAAZAPHENALENE, TRI-1,3,5-TRIAZINE]†

A. I. Finkel'shtein and N. V. Spiridonova

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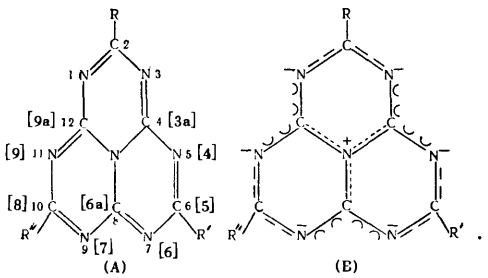
I. INTRODUCTION

The system of atoms (A), comprising six carbon and seven nitrogen atoms, has been called[1] "sym-heptazine".



(A) (B)

The type of delocalisation of the π electrons of the ring and their interaction with the p electrons of the central nitrogen atom are reflected in the structural formula (B), in which a provisional system of additional symbols[2] is used to represent the case in which there is no interaction between the sym-heptazine nucleus and the substituents R. This case is discussed, with the aid of quantum mechanics, by Pauling and Sturdivant[3], who were the first to propose a structural formula of type (A) for these compounds. According to them, the order of the C–N bond is nearly 1.50 for those farthest from the centre of the molecule (like 1–2, 2–3, 6–7, etc.), 1.36 for those nearer the centre (3–4, 4–5, 7–8, etc.), and 1.28 for the central bonds. These values correspond to interatomic distances, determined from isohybrid correlation curves[4], of 1.33, 1.35, and 1.37, respectively, which agree with the values given by Pauling and Sturdivant.

† The term introduced by Russian workers[1] is retained in this translation, but the "Ring Index" gives "tri-*s*-triazine" as a preferred trivial name; the systematic numbering is indicated in square brackets on formula (A) (Ed. of Translation).

Derivatives of sym-heptazine with substituents of the type R = R′ = R″ = NH_2 and OH (melem and cyameluric acid respectively) have been known for a very long time. Melem was first obtained by Liebig[5] in 1834, and cyameluric acid by Henneberg[6] in 1850.

Since then these compounds were forgotten for a long time, and have again attracted the attention of investigators only recently. Nevertheless our knowledge of this unusual class of organic compounds is very limited. In particular, free sym-heptazine (R = R′ = R″ = H) has not yet been synthesised, and other derivatives have been studied very little. The only practical applications known are a patent on the use of cyameluric and hydromelonic acids and their salts in photography[7] and a patent on the preparation of resins from melem[8], which have not received any widespread attention.

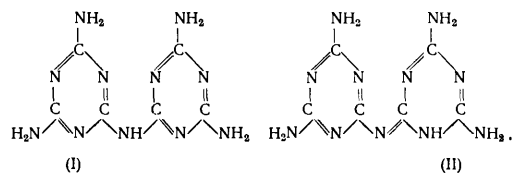
However, there is no doubt that this class of compounds holds promise. It is known, for example, that very many of them have high thermal stability, withstanding temperatures up to red heat without decomposition. At the same time these substances display a great variety of chemical properties, connected with the possibility of changing easily the nature of the substituents R, R′, and R″.

In this review the chemical and physicochemical properties of sym-heptazine derivatives are discussed with the aim of attracting investigators to greater study and application of this class of compounds.

2. DOES MELAM EXIST?

When melamine is heated at atmospheric pressure to 320°, deamination occurs to give a product which is almost insoluble in water and sparingly soluble in acids and alkalis.

Up to the present it has been considered[9,10] that the low-temperature deamination product is formed by the elimination of one molecule of ammonia from two molecules of melamine. Liebig called this product melam[11]. The structural formula (I) was proposed for melam by Klason[11], and has been adopted by recent workers[13].



(I) (II)

The ultraviolet absorption spectrum of the low-temperature deamination product of melamine in alkaline medium[14] has an absorption band at λ_{max} = 285 mμm, whereas in the spectrum of melamine the band of longest wavelength has λ_{max} = 236 mμm. This sharp difference in the absorption spectra cannot be explained on the basis of structural formula (I), in which the two 1,3,5-triazine rings can interact only comparatively weakly through the two C–N single bonds. An attempt was therefore made to explain this result by modifying formula (I) to formula (II).

An examination of infrared spectra[15] showed formula (II) also to be unsuitable, in view of the absence from the spectrum of the deamination product of the band at 1560 cm^{-1} which is characteristic of all compounds containing a 1,3,5-triazine ring of benzenoid structure[16]. Instead of this band, absorption bands were observed at 1615, 1435, and

795 cm^{-1}, and these are characteristic of sym-heptazine derivatives (see below).

Special work was undertaken[17] to settle finally the question of the mechanism of the thermal decomposition of melamine. At the suggestion of V. G. Zavarov, a determination was made not only of the amount of ammonia liberated but also of the melamine which had reacted. Many authors[12,18] did not carry out the latter determination, and so obtained erroneous results, since the decomposition of melamine was not complete.

This work[17] showed the molar ratio of melamine which had reacted to ammonia liberated to be 1 : 1, not 1 : 0.5, as would be expected for melam. The ratio of 1 : 1 indicates that the low-temperature product of the deamination of melamine is melem, and not melam. Melam is formed neither by the decomposition of melamine nor by that of cyanamide or dicyandiamide[17].

Ratios less than 1 : 1 obtained by other workers[18] are explained by disregard of the melamine in the reaction product.

Why does deamination not go to completion?

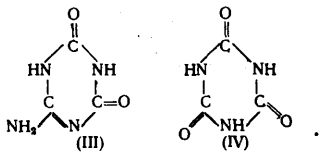
The observed phenomena can be explained on the assumption that deamination can proceed at a considerable rate only in the liquid phase. The process therefore begins at a temperature somewhat below the melting point of melamine (354°) because a small admixture of the reaction products lowers the melting point of the mixture. As the amount of melem increases, the melting point of the mixture passes through a minimum near 320° and then rises, the mixture solidifies, and deamination is retarded. At a higher temperature the mixture of melamine and melem solidifies at a larger melem content, and more complete deamination is therefore achieved under these conditions. In the presence of readily fusible compounds (*e.g.* dicyandiamide) the melting point of the mixture is lowered, and formation of melem begins at a lower temperature.

We may thus conclude that melam is not formed spontaneously in Nature, although it can probably be synthesised artificially‡.

3. MELEM

Two methods of preparing melem are known — (1) pyrolysis of ammonium thiocyanate below 260°,[5] and (2) thermal decomposition of melamine, dicyandiamide, and cyanamide[9,10,17].

Melem is[19] an amorphous white powder, sparingly soluble in water and in dilute acids and alkalis. Its solubility in acids and alkalis is 2–3 times as great as in water, and it can therefore be purified by dissolving it in a dilute acid and precipitating it by neutralisation. Boiling with 4 *N* potassium hydroxide gives cyameluric acid (R = R′ = R″ = OH), while on prolonged boiling in more concentrated alkalis the sym-heptazine ring breaks down and ammelide (III), a derivative of 1,3,5-triazine, is formed.



Under milder conditions melem can give[20] mixed amino- and hydroxy-derivatives of sym-heptazine, which can be regarded as amides of cyameluric acid — a monoamide (R = NH_2; R′ = R″ = OH) and a diamide (R = R′ = NH_2; R″ = OH).

Melem is considerably more stable in acids, and withstands brief boiling with nitric or hydrochloric acid[21]. On being heated to a high temperature in acids, it decomposes to cyanuric acid (IV) *via* intermediate products.

Melem is an amphoteric compounds with very weak acidic and alkaline properties, the latter somewhat predominating (the dissociation constants are given in Table 1). It is a by-product in the synthesis of melamine from dicyandiamide and can be present in significant quantities not only in the crude material but also in the recrystallised product[14].

The molecular structure of melem has been studied from infrared and ultraviolet spectra. In the infrared spectrum[15,22] three absorption bands characteristic of the sym-heptazine ring are observed, at 1605, 1475, and 802 cm^{-1} (Fig. 1). The infrared spectrum of deuteromelem[15] confirms this assignment. In the region of NH-stretching frequencies a spectrum characteristic of amides is observed: three diffuse absorption bands (3403, 3336, and 3103 cm^{-1}) indicate the presence of strong intermolecular hydrogen bonds and strong interaction between the amino-groups and the ring.

The ultraviolet spectrum of melem[23] and its ionic forms is shown in Fig. 2. The absorption spectrum of the neutral form is characterised by two intense absorption bands with maxima at 240 and 222 mμm. As expected, the intense bands of melem are displaced towards longer wavelengths in comparison with the corresponding 1,3,5-triazine derivative, which has a maximum[24] at 206 mμm.

TABLE 1.

Compound	Dissociation constants	Values from Refs. 1 and 23	Values from Ref. 27
Melem	Kb_1	10^{-12}	none
	Kb_2	$6\cdot10^{-14}$	»
	Kb_3	10^{-16}	»
	Ka_1	$2.5\cdot10^{-13}$	»
2,6-Diamino-10-hydroxy--sym-heptazine	Kb_1	$1.2\cdot10^{-12}$	none
	Kb_2	$2.5\cdot10^{-15}$	
	Ka_1	$7.9\cdot10^{-13}$	
	Ka_2	10	
2-Amino-6,10-dihydroxy--sym-heptazine	Kb_1	$6\cdot10^{-13}$	none
	Ka_1	$3.2\cdot10^{-7}$	
	Ka_2	$1.2\cdot10^{-9}$	
Cyameluric acid	Ka_1	$8.7\cdot10^{-4}$	10^{-3}
	Ka_2	$5.6\cdot10^{-7}$	$6.3\cdot10^{-7}$
	Ka_3	$4.6\cdot10^{-10}$	$1.2\cdot10^{-9}$
Hydromelonic acid	Ka_1	10	none
	Ka_2	$1.4\cdot10^{-3}$	$3.16\cdot10^{-3}$
	Ka_3	$7.7\cdot10^{-6}$	$1.26\cdot10^{-5}$

‡ *Note added in proof*. After this review had been written we became aware of a paper by Takimoto[33] showing that an extremely small quantity of melam is, nevertheless, formed in the decomposition of melamine. A method of preparing alkyl derivatives of melam from chloroalkyl derivatives of 1,3,5-triazine has been described recently[34]. A check made by us showed that this method is well reproducible and that the spectra of the compounds obtained agree with the spectra of melam given by Takimoto[33].

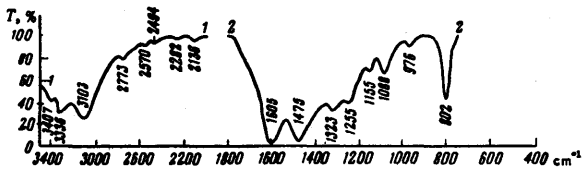


Fig.1. Infrared absorption spectrum of melem: 1) 1%, LiF prism; 2) 1%, NaCl prism (IKS-14).

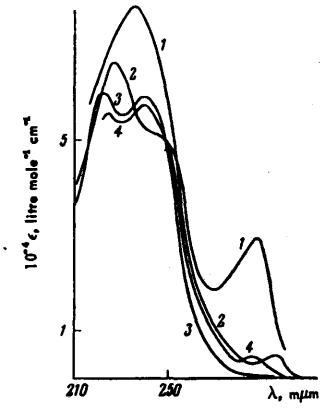
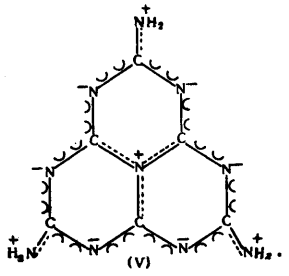


Fig.2. Ultraviolet spectra of melem at pH: 1) -1.7; 2) 1.1; 3) 7.0; 4) 14.0.

In addition to strong absorption in the 210–250 mμm region, there is comparatively weak absorption, in the spectra of the singly ionised and protonated forms, at 296 and 285 mμm respectively. The bands are very convenient for analysis, as they permit melem to be determined in a mixture with other derivatives of sym-heptazine and 1,3,5--triazine.

A detailed examination of the molecular structure of melem leads[15] to the structural formula (V).

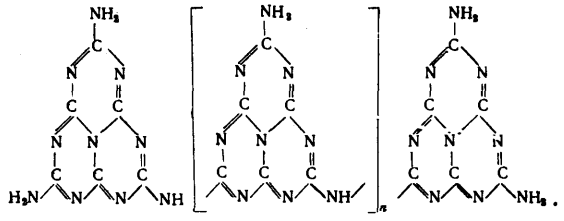


(V)

Melem is thermally stable, withstanding heating up to 450° without noticeable change. At higher temperatures it partly decomposes, forming melon and evolving ammonia, nitrogen, and cyanogen[19]. It is converted into melamine by the action of ammonia under pressure at a high temperature[19].

4. MELON — THE MATERIAL OF PHAROAH'S SERPENTS

When mercury thiocyanate is heated, fantastic structures are formed which remotely resemble a cluster of snakes ("Pharoah's serpents") and consist of the yellow substance melon, a name given to it by Liebig[5,25], who obtained melon by thermal decomposition of ammonium thiocyanate, melamine, and melem. The study of melon was continued by Klason[12] and Franklin[26]. Redemann and Lucas[13] proposed for melon a polymeric type of structural formula consisting of a number of sym-heptazine rings linked through nitrogen atoms (secondary amino-bridges).



An examination has been made[22] of the infrared spectra of specimens of melon obtained by thermal decomposition of melamine, "pseudothiocyanogen", ammonium thiocyanate, and mercury thiocyanate. These spectra (Fig. 3) were found to be identical, and therefore melon is a pure substance. A comparison of the spectra of melon and melem in the region of the lattice vibrations shows their great similarity, which supports the hypothesis[13] that melon is based on sym-heptazine rings. The greatest differences in the spectra are connected with the absorption bands of the NH bonds. A consideration of the nature of these bands[22] showed that the sym-heptazine rings are linked through secondary amino-bridges.

Absorption bands which might be assigned to 1,3,5--triazine rings were not found; May's suggestion[18] that these rings may be present in melon is therefore rejected. However, bands characteristic of 1,3,5-triazine are present in the thermal decomposition products of ammelide and ammeline.

Chemical properties also confirm the similarity of the molecular structures of melem and melon. Thus, hydrolysis of both compounds in alkalis gives cyameluric acid, and fusion with potassium thiocyanate yields hydromelonic acid (see below).

Melon is almost insoluble in water and in dilute acids and alkalis. It is thermally stable up to red heat.

It would be interesting to examine the possibility of using melon as catalyst, absorbent, ion-exchange resin, etc., but no work has yet been done on this.

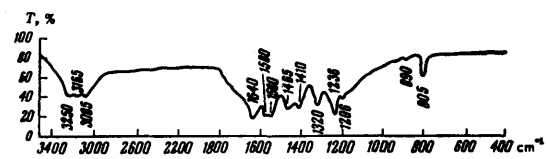
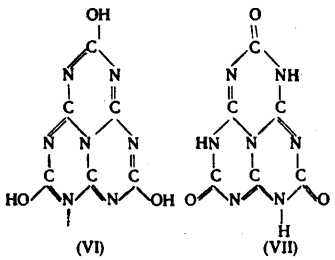


Fig.3. Infrared spectrum of melon in KBr.

5. CYAMELURIC ACID, ITS SALTS AND AMIDES

As already noted, hydrolysis of melem in alkalis gives salts of cyameluric acid (R = R′ = R″ = OH). This acid was first isolated by Henneberg[6], who ascribed to it the formula $H_3C_6O_3N_7$. The molecular structure was investigated further by Klason[12] and Franklin[26], who proposed various structural formulae, but it was only in 1937 that Pauling and Sturdivant[3] suggested the correct structural formula (VI), which is consistent with its chemical properties[27]. The choice between the hydroxy- and oxo--forms [structural formulae (VI) and (VII)] is an important question, studied in various instances by Sheinker[28], who showed that the substance usually exists as the oxo-form, but when formation of the hydroxy-form involves a large gain in energy owing to conjugation of bonds, either a tautomeric equilibrium is observed or the hydroxy-form predominates. The parallelism betwen cyameluric acid and cyanuric acid (IV) in such chemical properties as the formation of salts (*e.g.* both acids give a cuprammonium salt) and chlorides goes a little way towards answering this question, for in these cases cyanuric acid forms derivatives of the hydroxy-form.

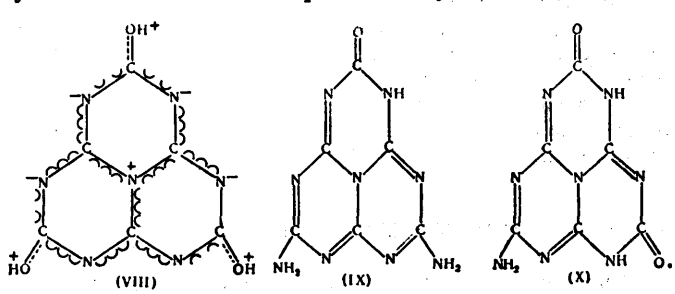


(VI) (VII)

cyameluric acid in the hydroxy-form — cyameluric acid in the oxo-form

Examination of physicochemical data is of greater importance. Thus, the magnetic susceptibility[29] supports structure (VI). The infrared spectra[15] (Fig. 4) show no bands which could be assigned to a carbonyl bond. The intense bands observed belong to the sym-heptazine ring.

This view is also confirmed by the ultraviolet spectra. Thus from Table 2, which gives data on the spectra of molecules and ions of amino- and hydroxy-derivatives of sym-heptazine[1], it is clear that there is a departure from the general regularity (in accordance with which an oxo--structure is expected) in the case of neutral cyameluric acid. A comparison of the spectra of melem and cyameluric acid[23] also supports the hydroxy-form. Thus, when the bond interaction is taken into account, the structure of cyamelluric acid can be represented by formula (VIII).



(VIII) (IX) (X)

Cyameluric acid is comparatively sparingly soluble in water[27]; its preparation from salts formed by the hydrolysis of melem is based on this property. Its dissociation constants are shown in Table 1. Salts of cyameluric

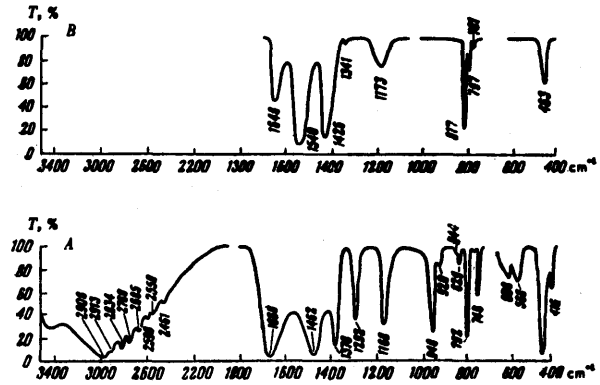
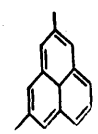
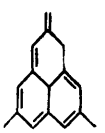
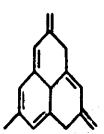
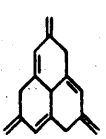


Fig.4. Infrared spectra of: *A*) cyameluric acid; *B*) potassium cyamelurate.

TABLE 2.

Arrangement of double bonds	Absorption bands	2,4,10-Triamino-sym-heptazine (melem)		2,6-Diamino-10-hydroxy-sym-heptazine		2-Amino-4,6,10-dihydroxy-sym-heptazine		2,4,10-Trihydroxy-sym-heptazine (cyameluric acid)	
	I	222	60 000	225	41 000	222	35 000	222	47 500
	II	240	59 000	250 shoulder	33 200	263 shoulder	18 300	250 shoulder	17 500
	III	—	—	—	—	—	—	—	—
	I	227	65 000	220	43 000	219,5	39 500	217	53 000
	II	245 shoulder	500 000	250 shoulder	weak	—	—	—	—
	III	296	4000	290	2200	285	6500	280	4500
	I	236	78 000	226	43 100	218	33 000	210	51 000
	II				—	—	—	—	—
	III	288	29 000	286	2800	380	7200	288	10 000
	I			229	39 500	215	33 000	208	48 000
	II			—	—	235 shoulder	198 000	235 shoulder	15 000
	III			228	530				

acid which have been described[13] are the tripotassium, trisodium, cuprammonium $CuNH_4(C_6N_7O_3).NH_3$, and mercury $Hg_3(C_6N_7O_3)$ salts. The first two are soluble in water, especially in hot water, and the other two are insoluble.

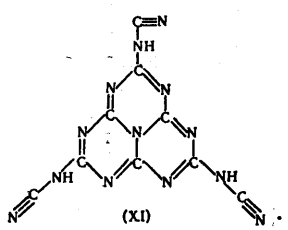
The triamide of cyameluric acid (melem) has already been described. The di- and mono-amides [(IX) and (X)] have been synthesised quite recently[20]. These substances are amorphous white powders, which decompose without melting at 350°. They are almost insoluble in water and organic solvents, but more soluble in mineral acids and alkalis, with which salts are formed. The molecular structure of the mono- and di-amides has been studied spectroscopically[1]. In contrast to cyameluric acid they

exist in the oxo-form. This is because formation of their oxo-forms is not accompanied by considerable disruption of the system of conjugated bonds.

The acid–base properties of the mono- and di-amides are given in Table 1. Ultraviolet spectral data for cyameluric acid and its amides are summarised in Table 2, in which data for the neutral molecules are located along the diagonal, those for negative ions above the diagonal (first, second, and third dissociation in sequence), and data for positive ions below the diagonal (in order of first, second, and third addition of protons).

6. HYDROMELONIC ACID

In 1835 Gmelin[30] obtained the tripotassium salt of hydromelonic acid by heating potassium ferrocyanide with sulphur. He also prepared other salts of hydromelonic acid, but was unable to establish its formula because of the inaccuracy of his analysis. Tripotassium hydromelonate was later obtained by Liebig[31] by dissolving melon in fused potassium thiocyanate. From numerous analyses of the potassium and silver salts Liebig established the empirical formula of hydromelonic acid as $C_9H_3N_{13}$. In 1886 Klason[12] suggested the structural formula $(C_3N_3)_3 \cdot (NH)_3N$, and in 1935 Franklin regarded hydromelonic acid as a derivative of hexamethylenetetramine. It was only in 1937 that Pauling and Sturdivant proposed the structural formula (XI), from the analogy between 1,3,5-triazine tricyanamide $C_3N_3(HNCN)_3$ and hydromelonic acid $C_6N_7 \cdot (HNCN)_3$.



(XI)

Hydrolytic decomposition of hydromelonic acid in acidic and alkaline media with formation of cyameluric acid, ammonia, and carbon dioxide confirms structure (XI). The ultraviolet[23] and infrared[15] spectra are also consistent with this structure, if bond interaction is taken into account. Thus, all three bands characteristic of the sym-heptazine ring are observed in the infrared spectrum (Fig. 5).

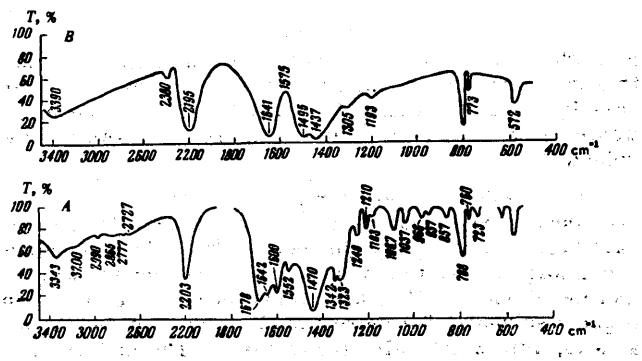


Fig.5. Infrared spectra of: *A*) hydromelonic acid; *B*) potassium hydromelonate.

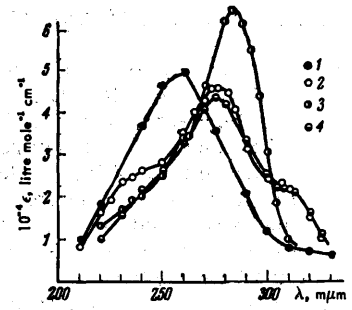


Fig.6. Ultraviolet spectra of hydromelonic acid at pH:
1) -2; 2) 0.7; 3) 7.0; 4) 9.0.

The C≡N frequency is here 2245 cm^{-1}, which is close to its value in acetonitrile (2249 cm^{-1}) and somewhat greater than in cyanamide. This is easily explained by the cyameluric acid nucleus being more electrophilic than the cyanide group and attracting the lone pair of electrons of the nitrogen atom. The frequency of the C≡N group in potassium hydromelonate (2180 cm^{-1}) is intermediate between the C≡N frequencies in cyanamide and the sodium salt of cyanamide

$$H_2\overset{+}{N}{=}{=}C{\overset{\smile}{=}}\bar{N},$$

and

$$Na^+[HN{=}{=}C{\overset{\smile}{=}}N^-]^-,$$

(2220 and 2096 cm^{-1}). This is explained by the negative charge on the nitrogen atom being partly transferred to the cyameluric nucleus, so that the state of the cyanamide nitrogen in the hydromelonate is closer to the state of this atom in cyanamide. There are two bands in the 1400–1700 cm^{-1} region of the spectrum of potassium hydromelonate, at 1655 and 1430 cm^{-1}. The latter band is characteristic of the cyameluric nucleus, just as a band at 1560 cm^{-1} is characteristic of a 1,3,5-triazine ring. The other band, at 1655 cm^{-1}, is apparently determined to a considerable extent by the nature of the outer part of the molecule.

The absorption band in the 802 cm^{-1} region (794 cm^{-1} in the spectrum of potassium hydromelonate) is also characteristic of derivatives of cyameluric acid. In the ultraviolet spectrum of the molecular-ion forms of hydromelonic acid (Fig. 6) the absorption maximum is shifted, as compared with melem, to longer wavelengths (250–290 mμm); this indicates a very strong interaction of the cyameluric ring with the nitrile group through two C=N bonds. There must then be a larger positive charge on the secondary amino-nitrogen atom, which facilitates N–H dissociation. Hydromelonic acid must therefore be regarded as a strong acid (Table 1).

7. OTHER DERIVATIVES OF sym-HEPTAZINE

Other derivatives of sym-heptazine are reported in only one paper[13].

1. Trichloro-sym-heptazine (cyameluryl trichloride) is prepared[13] by the reaction of potassium cyamelurate with phosphorus pentachloride in a sealed tube at 100–139°.

After removal of phosphoryl chloride and potassium chloride, a light yellow powder remained which was insoluble in organic solvents (chloroform, anisole, nitrobenzene, acetonitrile, and *o*-dichlorobenzene were tested). The substance does not melt but it sublimes (probably with partial oxidation). Cyameluric acid can be used in place of potassium cyamelurate for the preparation of trichloro--sym-heptazine.

2. *NN'N"*-Tribenzyl-sym-heptazine *NN'N"*-tribenzyl cyamelurate)is formed[13] by the interaction of equimolecular quantities of sodium cyamelurate and chlorobenzene in a sealed tube at 100° for 24 h, followed by heating at 156° for 12 h. Extraction with benzene and further recrystallisation from ethanol gives colourless needle-shaped crystals which melt at 283–284°.

Saponification with aqueous potassium hydroxide gives *N*-benzylbenzamide, indicating that an *N*-derivative of sym-heptazine had been formed.

3. Trimethyl-sym-heptazine is obtained[13] by treating cyameluric acid twice with excess of diazomethane. The chemical and physicochemical properties of this substance have not been studied.

No reports of the preparation of other derivatives of sym-heptazine are available to us.

It is clear from this review that derivatives of sym--heptazine are among the least studied classes of organic compounds. Apart from two patents, no use has yet been made of these compounds. In contrast to derivatives of 1,3,5-triazine, which have been widely used for a comparatively long time in various branches of industry and in agriculture, the potential of sym-heptazine derivatives has not been fully exploited. Their present position is comparable to that of 1,3,5-triazine derivatives 10–15 years ago.

Can one regard the use of these compounds in industry and agriculture as promising? In our opinion, one can. The stability of the sym-heptazine nucleus give confidence that derivatives will be used for the production of thermostable plastics, as catalysts for processes taking place at 300–400°, etc.

The strong interaction of the sym-heptazine ring with amino- and hydroxy-groups makes them highly polar, and this, together with the low solubility of these compounds, suggests possible use as adsorbents and ion-exchange resins. The high nitrogen content (up to 70% in some cases) indicates the possibility of using sym-heptazine derivatives in agriculture. The similarity in chemical structure of sym-heptazine derivatives to a number of physiologically active (including anticarcinogenic) substances suggests that they may be useful in pharmacology.

There is thus good reason to expect a brisk development of research furthering the application of this promising class of organic compounds, and it will not be surprising if derivatives of sym-heptazine are produced on a large scale in industry in the very near future.

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RUSSIAN CHEMICAL REVIEWS
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DIENE SYNTHESIS WITH DIENOPHILES CONTAINING HETERO-ATOMS

Yu. A. Arbuzov

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I. INTRODUCTION

Diene synthesis consists in the addition of a double or triple bond in a compound termed the dienophile to conjugated dienes having a *cis* arrangement of their double bonds, addition occurring at the 1,4 positions to form a six-membered ring[1-8].

The dieneophiles used comprise compounds containing an ethylenic and acetylenic bond, azo-compounds, nitroso--compounds, *N*-sulphinylamines and *N*-sulphinylamides, carbonyl and thiocarbonyl compounds, nitriles, azomethines, imidoyl chlorides, and quaternary immonium salts.

Study of the reactions of 1,3-dienes with dienophiles of different structures has shown that conjugation of the double or triple bond of the dienophile with electron-acceptor groups enhances, while conjugation of the multiple bond of the dienophile with electron-donor substituents diminishes the reactivity of the dienophile. On the other hand, electron-donor substituents enhance, while electron-acceptor substituents diminish the reactivity of the diene. Consequently dienophiles are electrophilic, and dienes nucleophilic, reagents[2,5-11].

The cause of the enhanced reactivity of dienophiles in which multiple bonds are conjugated with electron-acceptor groups is not the displacement of electrons in the same direction in the dienophile molecules, but a decrease in electron density on their multiple bonds. Investigations have shown that the reactivity of dienes and dienophiles depends also on their geometrical configuration[2,7-9,11,12].

The stereochemical and structural orientation of diene synthesis is of great interest[2,5,8,12]. It has been established that the position of the substituents with respect to the ring in the Diels–Alder adducts is the same as it had

been relative to the double bond in the dienophile. Hence *cis* addition takes place with respect to the dienophile. This also occurs with respect to the diene, as is indicated by the cyclic structure of the adducts. Finally, reaction can take place sterically in two ways, substituents in the dienophile being located in the adduct either on the same side as the cyclic double bond (*endo* position) or on the opposite side from the double bond (*exo* position). The *endo* adducts are usually formed.

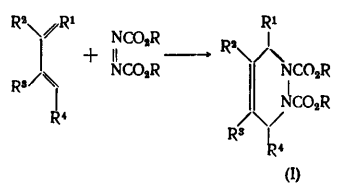
Structural isomers can be formed when 1- and 2-substituted dienes condense with unsymmetrical dienophiles. A vast amount of information has accumulated on the structural orientation of diene synthesis. Experiments have shown that it is affected by steric and polarisation factors. In several cases, however, it has been found that these factors do not determine the reaction sequence [2,7,12,13].

The steric and structural direction of diene condensations is obviously governed by the geometrical configuration of the transition state. However, there is at present no generally accepted view of the mechanism of diene synthesis, and its steric and structural orientation have not yet received a satisfactory theoretical explanation [7,12-18].

The present paper deals with diene syntheses involving dienophiles containing hetero-atoms. The literature published up to 1st March 1964 has been covered.

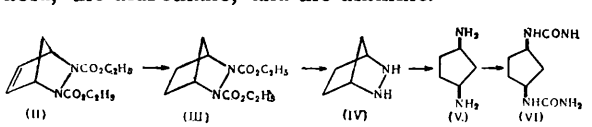
II. DIENE SYNTHESIS WITH AZO-COMPOUNDS

In 1925 Diels found [19,20] that azodicarboxylic esters† add on to conjugated dienes at the 1,4 positions to form dialkyl 1,2,3,6-tetrahydropyridazine-1,2-dicarboxylates (I):



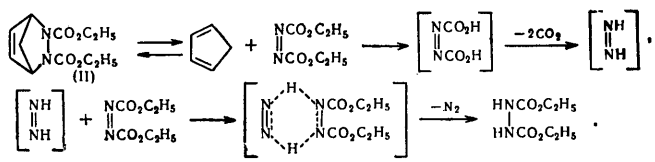
(I)

Diels obtained the adduct (II) by the interaction of diethyl azodicarboxylate with cyclopentadiene. The reaction took place in ethereal solution and was accompanied by the evolution of much heat, the adduct being obtained in high yields (90–95%). Diels established the structure of the adduct (II) by reducing it catalytically to the dihydro--derivative (III), saponification of which with alcoholic alkali gave the hydrazo-compound (IV). This was reduced with tin and hydrochloric acid to cyclopentane-*cis*-1,3-diamine (V), which was identified by conversion into the *cis*-1,3-diureido-derivative (VI), obtained by an alternative synthesis from cyclopentane-*cis*-1,3-dicarboxylic anhydride *via* the dimethyl ester, the dihydrazide, the diazide of the acid, the diurethane, and the diamine.

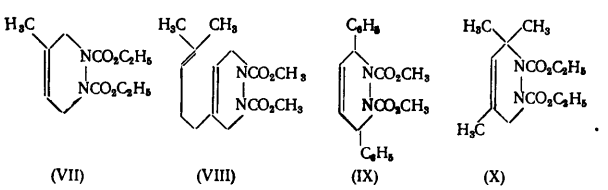


(II) (III) (IV) (V) (VI)

Stille has recently found [23] that hydrolysis of the adduct (II) with 10% hydrochloric acid yields hydrazodicarboxylic ester, the reaction probably involving the stages — (1) breakdown of the adduct into its original components, (2) partial hydrolysis of the azodicarboxylic ester to the acid, (3) decarboxylation of this acid to form reactive diimide, and (4) reduction by the diimide of the unhydrolysed portion of the azodicarboxylic ester, by a cyclic mechanism, to give the hydrazodicarboxylic ester:

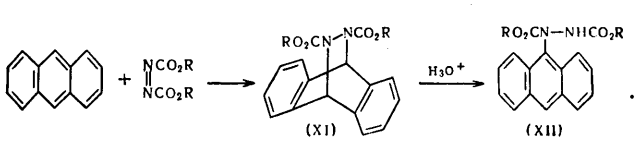


Diels obtained the adduct (VII) by reaction of diethyl azodicarboxylate with isoprene; the adducts (VIII) and (IX) were formed on reaction of dimethyl azodicarboxylate with myrcene [7-methyl-3-methyleneocta-1,6-diene] and with *trans*-1,*trans*-4-diphenylbutadiene. Diels assigned the structure of a 1,4 adduct (X) to the product obtained from diethyl azodicarboxylate and 2,4-dimethylpentadiene.



(VII) (VIII) (IX) (X)

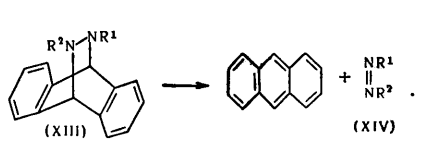
In 1938 Diels showed [24] azodicarboxylic esters react with anthracene in boiling toluene to form adducts (XI). In acid medium these adducts undergo isomerisation to form products, the structure of which was established by Alder [25] in 1954 as (XII).



(XI) (XII)

(*a*) R=CH_3; (*b*) R=C_2H_5.

In 1962 Corey and Mock found [26] that hydrolysis of the adduct (XI*b*) with alcoholic alkali at 25° yields 9,10-hydrazo-9,10-dihydroanthracene (XIII*a*), which on being heated dissociates into anthracene and diimide (XIV*a*). The compound (XIII*a*) has been used for the stereospecific reduction of double bonds. Thus deuteration of maleic and fumaric acids by means of the (XIII*a*)–deuterium oxide–dioxan system at 85° gave respectively *meso*- and (±)-2,3-dideuterosuccinic acid, in conformity with results of the diimide reduction of double bonds with other reducing systems [27-29].



(XIII) (XIV)

(*a*) $R^1=R^2=H$; (*b*) $R^1=H$, $R^2=CO_2C_2H_5$; (*c*) $R^1=CN$, $R^2=CO_2C_2H_5$.

In 1963 Harley-Mason reported [30] that on alkaline saponification of the adduct (XI*b*) the monodecarboxylated compound (XIII*b*) was formed as well as hydrazodihydroanthracene (XIII*a*). With cyanogen bromide, (XIII*b*) gave the

† For the *cis-trans* configuration of azodicarboxylic esters, see Refs. 21 and 22.

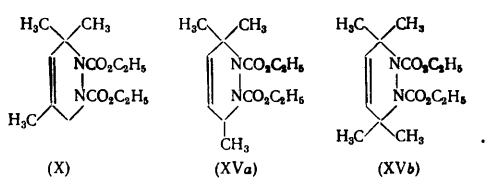
N-cyano-derivative (XIII*c*), which on being heated in a vacuum decomposed into anthracene and the cyano-ester (XIV*c*). This last compound proved to be an extremely reactive dienophile, adding on readily to anthracene to form the adduct (XIII*c*), and reacting with 1,4-diphenylbutadiene with the evolution of heat.

The reaction of azodicarboxylic esters with 1,3-dienes, discovered by Diels and leading to the formation of "diene" adducts (I), has been investigated by several workers. Adducts have been obtained from azodicarboxylic esters with butadiene[25,31-37], isoprene[32,33,35], pentadiene[32,33,35], 2,3-dimethylbutadiene[32,33,35,38], hexa-2,4-diene[32,33,35,39], 2-methylpentadiene[31], 3-methylpentadiene[35], 1-methoxybutadiene[40], 2-chlorobutadiene[40], cyclopentadiene[31,34,41-44], cyclohexadiene[39,45,46], 1,1′-bi(cyclopentenyl)[35], 1,1′-bi(cyclohexenyl)[47], 1-arylbutadienes[33,48-50], 1-phenylpentadiene[33,51], 1,4-diphenylbutadiene[25,31,33,49,51,52], anthracene[31], 2-chloroanthracene[53], ethyl sorbate[38], furan[34,54], 2-methylfuran[54], furfurylidene diacetate[25], 2,3-benzacridine[55], 5,6-dimethylenebicyclo[2,2,1]hept-2-ene[47], bicyclo[4,2,0]octa-2,4-diene[56], and 1-8-octamethylbicyclo[4,2,0]octa-2,4,7-triene.[57,58]

Rodgman and Wright[41] made a kinetic study of the reaction between azodicarboxylic esters and cyclopentadiene, and found it to be of the second order overall and the first order with respect to each reactant.

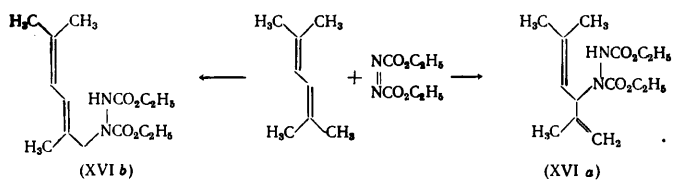
It has recently been found that, if the 1,4 positions in dienes are strongly substituted, reaction with azodicarboxylic ester takes place by a mechanism not of diene synthesis but of substitutive addition.

In 1957 Levina and her collaborators[35] obtained addition products from azodicarboxylic ester with 2,4-dimethylpentadiene, 2-methylhexa-2,4-diene, and 2,5-dimethylhexa-2,4-diene, and ascribed to them the formulae (X), (XV*a*), and (XV*b*).



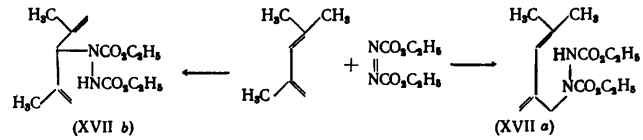
(X) (XV*a*) (XV*b*)

It was later found[59] that the reaction of these dienes with azodicarboxylic ester involves substitutive addition with the formation of monosubstituted derivatives of hydrazodicarboxylic ester. In 1962 Gillis and Beck[38] established that interaction between azodicarboxylic ester and 2,5-dimethylhexa-2,4-diene involves 85% of indirect substitutive addition with formation of the adduct (XVI*a*) and 15% of direct substitutive addition with formation of the adduct (XVI*b*):



(XVI *b*) (XVI *a*)

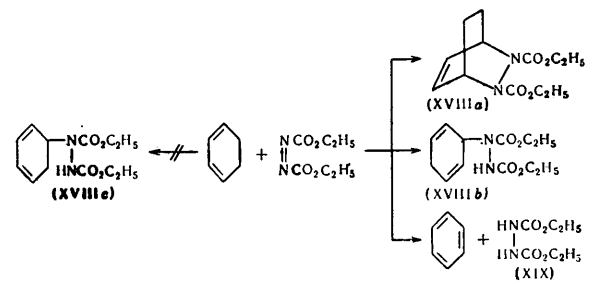
It was further shown[47] that azodicarboxylic ester adds on to 2,4-dimethylpentadiene by indirect substitutive addition to form isomeric adducts (XVII*a*) and (XVII*b*) in the proportions 4 : 1:



(XVII *b*) (XVII *a*)

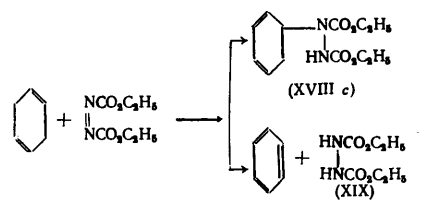
It has recently been found that cyclohexadiene and cycloheptatriene undergo substitutive addition with azodicarboxylic ester.

As early as 1935 Pirsch[45] described the synthesis of the adduct (XVIII*a*) from cyclohexadiene and azodicarboxylic ester. In 1962 Cohen[39] repeated this synthesis, and found that the product of the reaction comprised a mixture of the 1,4 adduct (XVIII*a*), a product of direct substitutive addition (XVIII*c*), and hydrazodicarboxylic ester. A little later it was found[38,60] that these reactants undergo indirect substitutive addition to form the adduct (XVIII*b*). Detailed investigation of the products has shown[46] that the reaction involves 80% of indirect substitutive addition to form (XVIII*b*), 5–15% of diene synthesis yielding (XVIII*a*), and 15–5% of oxidation–reduction with the formation of benzene and hydrazodicarboxylic ester (XIX):



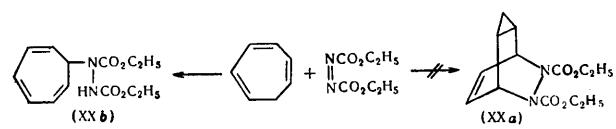
(XVIII *c*) (XVIII *a*) (XVIII *b*) (XIX)

It has been found that cyclohexa-1,4-diene, too, reacts with azodicarboxylic ester in two ways, to form the adduct (XVIII*c*), and benzene and hydrazodicarboxylic ester (XIX)[46,60]:



(XVIII *c*) (XIX)

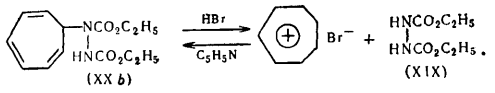
In 1961 Cinnamon and Weiss[61] investigated the reaction between azodicarboxylic ester and cycloheptatriene. This hydrocarbon does not usually react with dienophiles as such, but first passes into bicyclo[4,1,0]hepta-2,4-diene by an intramolecular Diels–Alder reaction[62-66]. It was therefore expected that an addition product of azodicarboxylic ester and bicycloheptadiene (XX*a*) would be formed. Examination of the ultraviolet and infrared spectra of the adduct, however, showed it to be a 7-substituted cycloheptatriene (XX*b*)‡:



(XX *b*) (XX *a*)

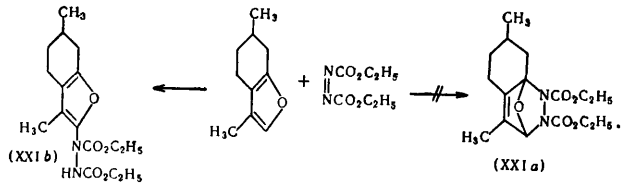
‡ Schenck[67] has found that the adduct (XX*b*) is also formed by the photochemical condensation of cycloheptatriene with azodicarboxylic ester.

The action of hydrogen bromide on an ethereal solution of the adduct (XX*b*) gave tropylium bromide and hydrazodicarboxylic ester (XIX); these products interact in the presence of pyridine to yield the adduct (XX*b*) again:



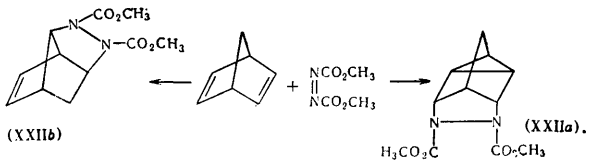
(XX *b*) (XIX)

In 1960 Häring[68] and Treibs[69] obtained from methofuran and azodicarboxylic ester an adduct for which the structural formulae (XXI*a*) and (XXI*b*) were possible. Examination of its ultraviolet and infrared spectra showed[69] that its structure was represented by (XXI*b*):



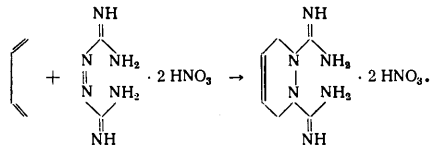
(XXI *b*) (XXI *a*)

In 1962 Cristol[70] found that dimethyl azodicarboxylate reacts at 150–160° with bicyclo[2,2,1]hepta-2,5-diene to form two crystalline 1 : 1 adducts melting at 60° and 110°. The latter product was regarded as a 2,6 adduct (XXII*a*) on the basis of an examination of the infrared and nuclear magnetic resonance spectra, from study of the chemical properties, and by analogy with addition products of other dienophiles with this hydrocarbon[71–74]. The isomeric adduct of m.p. 60° probably has the structure (XXII*b*). Bicycloheptadiene yields two 1 : 1 adducts with diethyl azodicarboxylate, too[70,75].



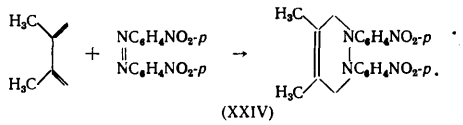
(XXIIb) (XXIIa).

In 1952 MacKenzie *et al.*[31] reported that azodicarboxamidinium dinitrate reacts with butadiene in the presence of pyridine to form the adduct (XXIII):



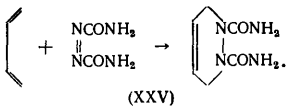
(XXIII)

In 1953 Baranger[32] found that *pp'*-dinitroazobenzene reacts at 150–160° with 2,3-dimethylbutadiene to form a 1,4 adduct (XXIV):



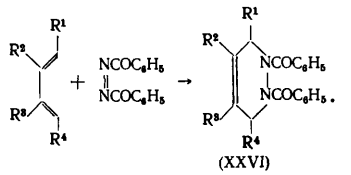
(XXIV)

Hunter[76] discovered that butadiene reacts with azodicarboxamide at 100° to form the adduct (XXV):



(XXV)

In 1959 Levina and her coworkers[77] showed that dibenzoyldiimide (azodibenzoyl) reacts at room temperature with 1,3-dienes to form 1,2-dibenzoyl-1,2,3,6-tetrahydropyridazines (XXVI):



(XXVI)

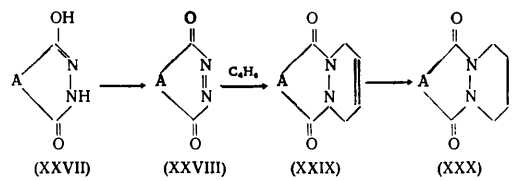
These workers subsequently established[78] that other diaroyldiimides (di-*p*-toluoyldiimide, di-*p*-anisoyldiimide, and *p*-anisoyl-*p'*-nitrobenzoyldiimide) react with 1,3-dienes to form 1,4 adducts.

2,4-Dimethylpentadiene undergoes substitutive addition with dibenzoyldiimide[78].

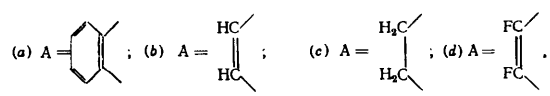
The reaction of diaroyldiimides with cyclopentadiene is of the second order overall, being of the first order with respect to each of the reactants[79].

During recent years it has been shown that cyclic diacyldiimides possess very high dienophilic activity.

In 1960 Clement[80] found that oxidation of phthalohydrazide (XXVII*a*) with lead tetraacetate yields the extremely unstable 1,4-dihydro-1,4-dioxophthalazine (XXVIII*a*). When oxidation was carried out in acetonitrile at 0°, a green solution of the dione was obtained, from which was isolated a colourless amorphous substance which proved to be a polymer of the dione. On addition of butadiene to the green solution, the colour immediately disappeared, and a Diels–Alder adduct (XXIX*a*) was formed. When oxidation of phthalohydrazide was carried out at 0° in the presence of butadiene, a 90% yield of (XXIX*a*) was obtained. The structure of this adduct was established by catalytic reduction to the dihydro-derivative (XXX*a*), and by alkaline hydrolysis to phthalic acid and 1,2,3,6-tetrahydropyridazine. Finally, the adduct was synthesised by condensing phthalic anhydride with 1,2,3,6-tetrahydropyridazine.



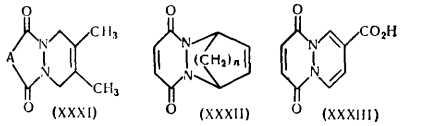
(XXVII) (XXVIII) (XXIX) (XXX)



In 1962 Clement[81] found that oxidation of maleohydrazide (XXVII*b*) and succinohydrazide (XXVII*c*) with lead tetraacetate in the presence of butadiene yields the respective adducts (XXIX*b*) and (XXIX*c*), catalytic reduction of both

of which gave the known 1,2-succinyl-1,2-diazacyclohexane (XXX*c*). The adduct (XXIX*b*) was synthesised by condensing 1,2,3,6-tetrahydropyridazine with maleic anhydride.

Kealy[82] suggested a convenient method for preparing the cyclic diacyldiimides (XXVIII*a–c*) by oxidising the potassium or sodium salts of the corresponding cyclic hydrazides at -77°. He found that the cyclic diacyldiimides, which he proposed to call diazaquinones, reacted rapidly in acetone solution at -77° with 1,3-dienes. Under these conditions 1,4-dihydro-1,4-dioxophthalazine (XXVIII*a*) reacts with butadiene and 2,3-dimethylbutadiene to form the adducts (XXIX*a*) and (XXXI*a*). Reaction of 3,6-dihydro-3,6-dioxopyridazine (XXVIII*b*) with butadiene, 2,3-dimethylbutadiene, cyclopentadiene, cyclohexadiene, and coumalic [6-oxopyran-3-carboxylic] acid yielded respectively the adducts (XXIX*b*), (XXXI*b*), (XXXII*a*), (XXXII*b*), and (XXXIII). 4,5-Difluoro-3,6-dihydro-3,6-dioxopyridazine (XXVIII*d*) and 2,3-dimethylbutadiene gave the adduct (XXXI*c*).

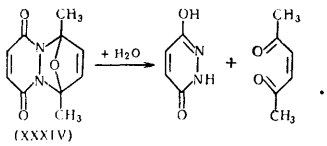


(XXXI) (XXXII) (XXXIII)

for (XXXI) (*a*) A = ; (*b*) A = ; (*c*) A = .

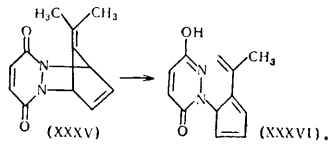
for (XXXII) *a*, *n* = 1; *n* = 2.

Furan and 2,5-dimethylfuran reacted readily with 3,6-dihydro-3,6-dioxopyridazine (XXVIII*b*), but the diene adducts could not be isolated. That produced from furan decomposed during isolation, while the adduct from 2,5-dimethylfuran (XXXIV) underwent hydrolysis on isolation, with the formation of maleichydrazide and hex-3-ene-2,5-dione:



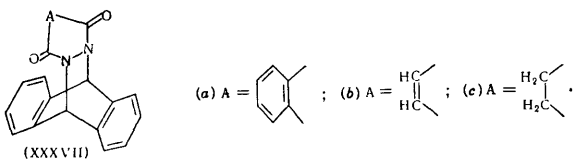
(XXXIV)

From (XXVIII*b*) and $\alpha\alpha$-dimethylfulvene a crystalline adduct (XXXV) was obtained, which gradually underwent rearrangement in the solid state, probably into the monosubstituted hydrazide (XXXVI):



(XXXV) (XXXVI).

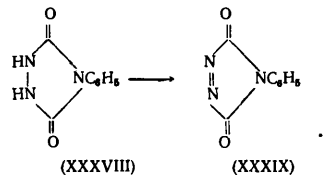
By oxidising the cyclic hydrazides (XXVII*a–c*) with lead tetraacetate in the presence of anthracene, Clement[81] obtained the Diels–Alder adducts (XXXVII*a–c*):



(XXXVII)

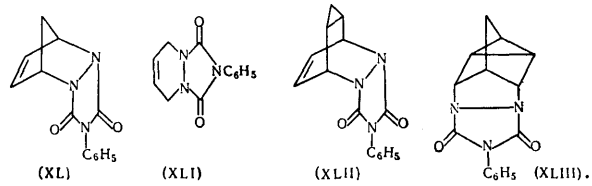
(*a*) A = ; (*b*) A = ; (*c*) A = .

In 1962 Cookson *et al.*[83] found that 3,5-dioxo-4-phenyl-1,2,4-triazolidine (XXXVIII) was oxidised by t-butyl hypochlorite in acetone medium at -78° to 3,5-dioxo-4-phenyl-1,2,4-triazoline (XXXIX):



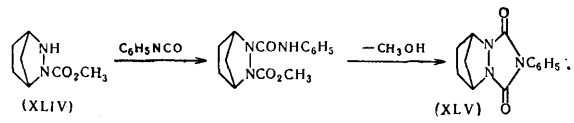
(XXXVIII) (XXXIX)

In acetone solution (XXXIX) reacts instantaneously with cyclopentadiene at -78°, and with butadiene and cycloheptatriene at -50°, to give high yields of the diene adducts (XL)–(XLII). With bicyclo[2,2,1]hepta-2,5-diene it gave a 1 : 1 adduct, which was assigned the 2,6-adduct structure (XLIII) on the basis of the infrared spectrum and by analogy with addition products of other dienophiles with bicycloheptadiene[71–74].



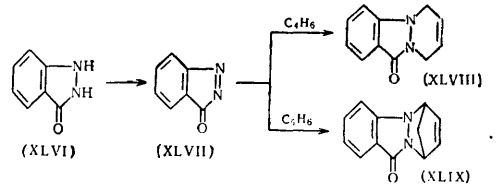
(XL) (XLI) (XLII) (XLIII).

The structure of the adduct (XL) was established by catalytic reduction to the dihydro-derivative (XLV), which was synthesised by the following reactions from the ester (XLIV), which had been obtained previously by Diels[19]:



(XLIV) (XLV)

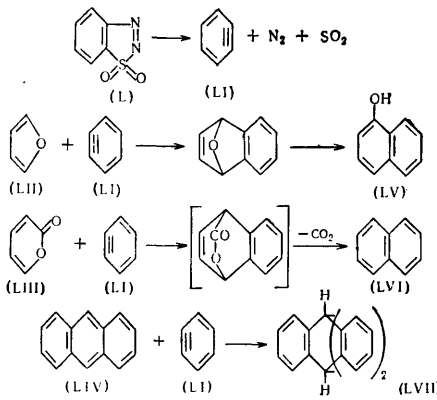
Ullman and Bartkus[84] oxidised 2,3-dihydro-3-oxoindazole (XLVI) in acetonitrile at -10° with lead tetraacetate to a green solution of the 3-oxoindazole (XLVII). On addition of butadiene or cyclopentadiene the colour of the solution at once disappeared, with formation of the Diels–Alder adducts (XLVIII) and (XLIX):



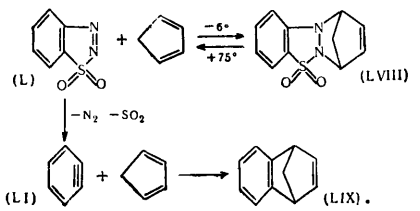
(XLVI) (XLVII) (XLVIII) (XLIX)

Wittig[85–88] diazotised sodium *o*-aminobenzenesulphinate at -15° and obtained the cyclic azo-sulphone (L) as yellow crystals which decomposed explosively at 60°. In solution (L) decomposes rapidly even at 10° to form dehydrobenzene [cyclohexadienyne] (LI), nitrogen, and sulphur dioxide. Decomposition of the azo-sulphone (L) in the presence of furan (LII), 2-pyrone (LIII), and anthracene

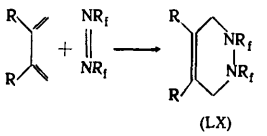
(LIV) gave respectively 1-naphthol (LV), naphthalene (LVI), and triptycene (LVII):



The azo-sulphone (L) reacts with acetonitrile medium at -6° with cyclopentadiene to form the Diels–Alder adduct (LVIII), which at 75° breaks down into the original components. When (LVIII) was decomposed in cyclopentadiene medium, the Diels–Alder condensation product (LIX) of dehydrobenzene (LI) and cyclopentadiene was obtained, and was identified as its adduct with phenyl azide.



In 1962 Chambers[89] observed that fluorinated azoalkanes react at elevated temperatures with 1,3-dienes to form the 1,2-bisfluoroalkyl-1,2,3,6-tetrahydropyridazines. Addition products were obtained from hexafluoroazomethane with butadiene and 2,3-dimethylbutadiene (LX*a*) and (LX*b*), from perfluoroazobutane and butadiene (LX*c*), and from 5*H*, 5′*H*-eicosafluoroazopentane and butadiene (LX*d*):



(LX)

(*a*) R=H, $R_f=CF_3$; (*b*) R=CH_3, $R_f=CF_3$; (*c*) R=H, $R_f=C_4F_9$;

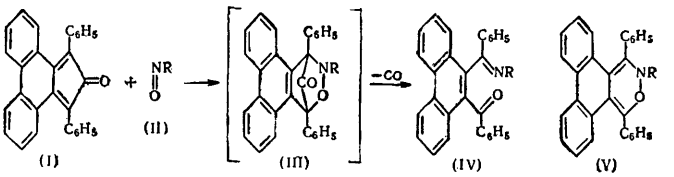
(*d*) R=H, $R_f=H(CF_2)_5$.

Examination of the infrared and nuclear magnetic resonance spectra of the addition products showed them to be Diels–Alder adducts (LX*a–d*). The ability of fluorinated azoalkanes to undergo diene condensation is explained by the electrophilic properties of fluoroalkyl groups, which cause a diminution in the electron density on the azo-group.

III. DIENE SYNTHESIS WITH NITROSO-COMPOUNDS§

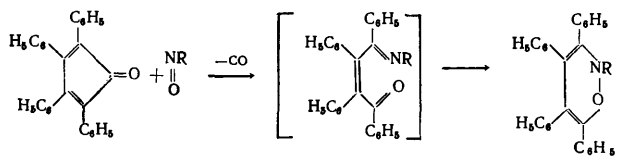
1. Reaction of Aromatic Nitroso-Compounds with Cyclones and 1,3-Diphenylisobenzofuran

During 1939–1940 Dilthey[90,91] studied the reaction of aromatic nitroso-compounds with cyclones. He found that phencyclone (I) and *NN*-dimethyl-*p*-nitrosoaniline (II*a*) interact in pyridine at room temperature to form the anil of 9,10-dibenzoylphenanthrene (IV*a*) and carbon monoxide. An unstable Diels–Alder adduct containing an *endo*-carbonyl bridge (III*a*) is probably first formed in this reaction, and decomposes under the experimental conditions into carbon monoxide and the anil (IV*a*). On treatment with acids, (IV*a*) rearranges into a 1,2-oxazine derivative (V*a*). Reaction of phencyclone (I) with nitrosobenzene (II*b*) gave the anil (IV*b*).



(*a*) R=$C_6H_4N(CH_3)_2$-*p*; (*b*) R=C_6H_5.

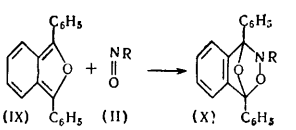
NN-Dimethyl-*p*-nitrosoaniline reacted with tetracyclone (VI) only on heating, and in this case the intermediate anil (VII) could not be detected. The product of the reaction was the 1,2-oxazine derivative (VII)¶.



(VI) (VII) (VIII)

R=$C_6H_4N(CH_3)_2$-*p*.

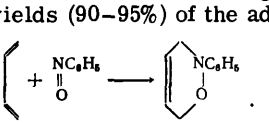
In 1949 Mustafa[94] reported that 1,3-diphenylisobenzofuran (IX) reacts in the presence of piperidine with *NN*-dimethyl-*p*-nitrosoaniline (II*a*) and nitrosobenzene (II*b*) to form the adducts (X*a*) and (X*b*), which at 270° decompose to regenerate the original 1,3-diphenylisobenzofuran:



(*a*) R=$C_6H_4N(CH_3)_2$-*p*; (*b*) R=C_6H_5.

2. Addition of Aromatic Nitroso-Compounds to 1,3-Dienes

In 1945 Khruleva[95] observed that nitrosobenzene reacts with butadiene to form a crystalline compound melting at 50°. In 1948 Arbuzov[96–98] established that the reaction is one of diene synthesis with the formation of 3,6-dihydro-2-phenyl-1,2-oxazine (I). The reaction goes smoothly at 0°, giving high yields (90–95%) of the adduct.



(I)

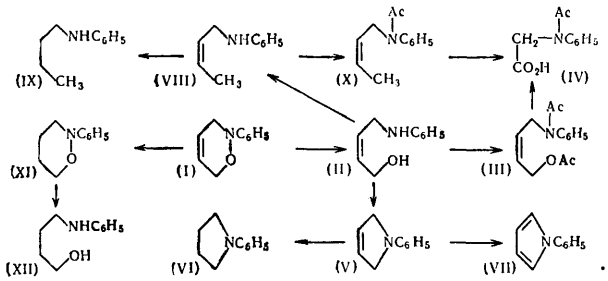
The structure of (I) was established by reducing the adduct with zinc and acetic acid to give the amino-alcohol

§ For the structure and properties of *C*-nitroso-compounds see Refs. 92 and 93.

¶ *Note added in proof*. Rigaudy[196] has recently established that this reaction product is an unsaturated γ-lactam, 1-*p*-dimethylaminophenyl-5-oxo-2,3,4,4-tetraphenyl-Δ^2-pyrroline.

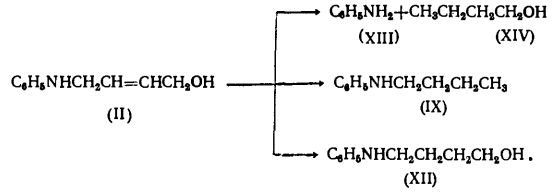
(II), which was converted into the diacetyl derivative (III), oxidation of this compound with potassium permanganate giving *N*-acetyl-*N*-phenylglycine (IV). Examination of the Raman spectrum of solutions of the adduct (I) in acetone or alcohol revealed the frequency of an isolated C=C bond [99].

The structure of the addition product of nitrosobenzene and butadiene was investigated also by Wichterle [100], but he reached the erroneous conclusion that it was 3,4-epoxy-1--phenylpyrrolidine.



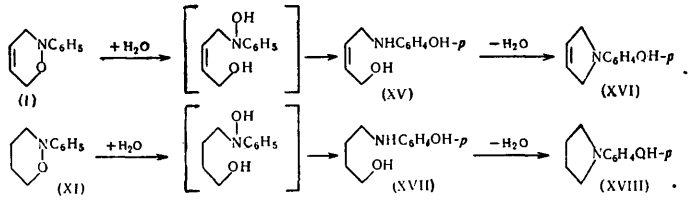
Interesting results were obtained from a study of the chemical transformations of the adduct (I). [101-103] On being heated with acids, the amino-alcohol (II) underwent cyclisation to 1-phenyl-Δ^3-pyrroline (V) catalytic reduction of which yielded 1-phenylpyrrolidine (VI). Oxidation of (V) with potassium permanganate gave 1-phenylpyrrole (VII). Reduction of (I) with sodium and alcohol resulted in *N*-but--2′-enylaniline (VIII), and catalytic reduction of this compound gave *N*-butylaniline (IX). Oxidation of the acetyl derivative (X) of (VIII) with potassium permanganate yielded *N*-acetyl-*N*-phenylglycine (IV). Catalytic reduction of the adduct (I) produced tetrahydro-2-phenyl-1,2--oxazine (XI), which was reduced with zinc and acetic acid to 4-anilinobutan-1-ol (XII).

Catalytic hydrogenation of the amino-alcohol (II) gave aniline (XIII), butan-1-ol (XIV), *N*-butylaniline (IX), and 4-anilinobutan-1-ol (XII). The main products of the reaction were aniline and butanol, whose formation is explained by initial hydrogenolysis of (II) to aniline and but-2-en-1-ol, the latter then being reduced to butanol. *N*-Butylaniline is probably formed by reduction of (II) to *N*-but-2′-enylaniline with subsequent reduction of the latter to *N*-butylaniline.

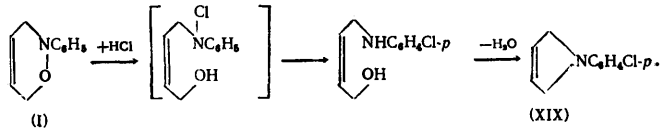


Wichterle [104] studied the reduction of the adduct (I) and of its dihydro-derivative (XI) with organomagnesium compounds. With ethylmagnesium bromide and some other organomagnesium compounds the adduct (I) gave 4-anilino-but-2-en-1-ol (II); 4-anilinobutan-1-ol (XII) was obtained from the dihydro-derivative (XI) and ethylmagnesium bromide.

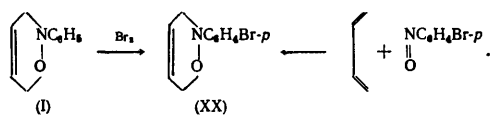
Later Wichterle [105] found that (I) and (XI) are hydrolysed by dilute phosphoric acid to the amino-alcohols (XV) and (XVII). More concentrated phosphoric acid results in cyclisation of these latter compounds to the amines (XVI) and (XVIII).



Kojima [106] showed that reaction of the adduct (I) with concentrated hydrochloric acid yields 1-*p*-chlorophenyl--Δ^3-pyrroline (XIX):



Kresze [107] found that bromination of the adduct (I) gave the hydrobromide of 2-*p*-bromophenyl-3,6-dihydro-1,2-oxazine. The base (XX) isolated from this hydrobromide was identical with the adduct prepared from butadiene and *p*-bromonitrosobenzene.

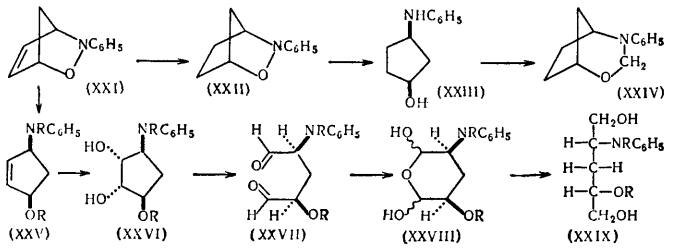


Arbuzov [108-111] investigated the reaction of butadiene with *o*-, *m*-, and *p*-nitrosotoluenes, and found from the structure of the adducts that in all cases the reaction was one of diene synthesis.

It was subsequently found that other 1,3-dienes, as well as butadiene, react with aromatic nitroso-compounds to form 2-aryl-3,6-dihydro-1,2-oxazines. Diels–Alder adducts have been obtained from aromatic nitroso-compounds and isoprene [112,113], pentadiene [94,114], 2,3-dimethylbutadiene [115-120], hexa-2,4-diene [108], cyclopentadiene [121-126], 5-methoxymethylcyclopentadiene [126], cyclopentadien-1--ylmethyl acetate [126], cyclohexadiene [123-125], cycloheptatriene [122,125], cyclooctadiene [125,127], 1,1′-bi(cyclohexenyl) [115], 1-arylbutadienes [115,125,128,129], 1,4-diphenylbutadiene [128], 2-chlorobutadiene [130,131], 2-methoxybutadiene [112], and ethyl sorbate [123].

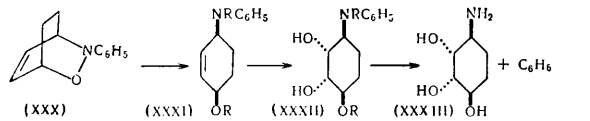
Thus by the action of nitrosobenzene on cyclopentadiene at 0° Kresze [121-124] obtained the unstable 1,4 adduct (XXI), from which an adduct with phenyl azide was obtained. Catalytic reduction of (XXI) at -5° yielded the dihydro--derivative (XXII) and *cis*-3-anilinocyclopentanol (XXIII). Condensation of the latter with formaldehyde resulted in a tetrahydro-1,3-oxazine derivative (XXIV). Reduction of (XXI) with zinc and acetic acid gave *cis*-4-anilinocyclopent-2-enol (XXV*a*), which was converted into the diacetyl derivative (XXV*b*). On oxidation of the latter with potassium permanganate, the 1,4-diacetyl derivative of 4-anilinocyclopentane-1,2,3-triol (XXVI*b*) was obtained, and this was further oxidised with lead tetraacetate to the diacetyl derivative of *erythro*-2-anilino-4-hydroxyglutaraldehyde (XXVII*b*), which was isolated as the internal hemiacetal of the monohydrate [tetrahydro-2,6-dihydroxypyran] (XXVIII*b*).

On reduction of this compound with sodium tetrahydroborate a 2,4-diacetyl derivative of 2-anilino-2,3-dideoxyerythritol [*sic*. 2-acetanilido-4-*O*-acetyl-2,3-dideoxyarabitol ? (Ed. of Translation)] (XXIX*b*) was formed.



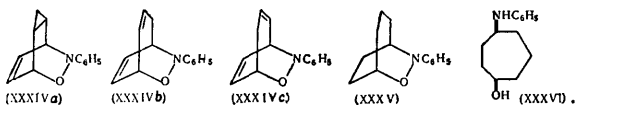
(*a*) R=H; (*b*) R=Ac.

By condensing nitrosobenzene with cyclohexadiene Arbuzov and Mastryukova [132] obtained the diene adduct (XXX), which was reduced to *cis*-4-anilinocyclohex-2-enol (XXXI*a*), and the latter converted into the diacetyl derivative (XXXI*b*). By oxidising (XXXI*b*) with potassium permanganate Kresze [123,124] obtained a 1,4-diacetyl derivative of 4-anilinocyclohexane-1,2,3-triol (XXXII*b*), which was saponified to the triol itself (XXXII*a*). Catalytic hydrogenolysis of the triol gave 4-aminocyclohexane-1,2,3-triol (XXXIII).



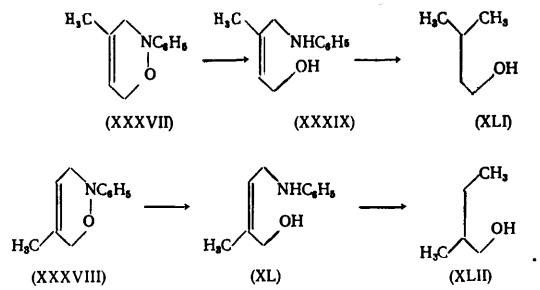
(*a*) R=H; (*b*) R=Ac.

An adduct for which the structural formulae (XXXIV*a–c*) were possible was obtained by Kresze [122] by the reaction of nitrosobenzene with cycloheptatriene. Structure (XXXIV*a*) was possible if the cycloheptatriene underwent isomerisation into norcaradiene (see p. 409). Examination of the nuclear magnetic resonance spectrum of the adduct and study of the chemical changes which it underwent eliminated the structure (XXXIV*a*) and were consistent with the other two structures. Catalytic reduction of the adduct resulted in the tetrahydro-derivative (XXXV), which gave *cis*-4-anilinocycloheptanol (XXXVI) on reduction with zinc and acetic acid.

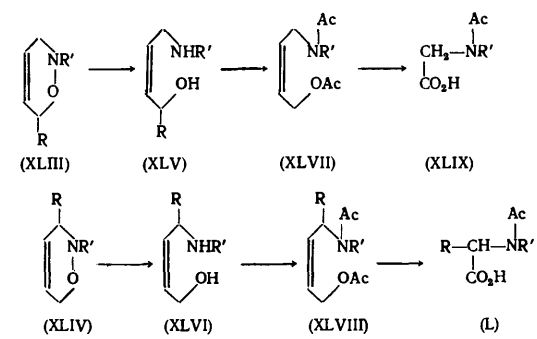


Arbuzov and his coworkers [112,114] investigated the structure of the addition products formed by nitrosobenzene with isoprene and with *trans*-pentadiene. When unsymmetrical dienophiles add on to 1- and 2-substituted 1,3-dienes, the order of addition usually agrees well with the direction of polarisation in both dienophile and diene. In several reactions with 1-substituted dienes, however, the results were inconsistent with the view that polarisation factors determine the structural orientation of diene synthesis [7,12].

It was expected that reaction of nitrosobenzene with isoprene would give the isomer (XXXVII) either alone or mixed with a smaller quantity of the isomer (XXXVIII). The structure of the adduct was established by reducing it with zinc and acetic acid, when these isomers should give the amino-alcohols (XXXIX) and (XL), and the latter on catalytic reduction should yield 3-methylbutanol (XLI) and 2-methylbutanol (XLII). In fact the amino-alcohol obtained by reduction of the adduct yielded only 3-methylbutanol (XLI) on catalytic hydrogenation, and hence the adduct has the structure (XXXVII).



Reaction of *trans*-pentadiene with nitrosobenzene could yield the isomers (XLIII*a*) and (XLIV*a*), reduction of which with zinc and acetic acid would give the amino-alcohols (XLV*a*) and (XLVI*a*), which could be converted into diacetyl derivatives (XLVII*a*) and (XLVIII*a*); these on oxidation with potassium permanganate should produce *N*-acetyl-*N*-phenylglycine (XLIX*a*) and *N*-acetyl-*N*-phenylalanine (L*a*). In fact, on application of the above series of reactions to the adduct, the amino-acids (XLIX*a*) and (L*a*) were isolated from the oxidation products in the proportions 1 : 3. It was thus established that the adduct consisted of a mixture of the isomers (XLIII*a*) and (XLIV*a*) with the latter predominating. Hence the polarisation factor does not determine the order of addition of nitrosobenzene to *trans*-pentadiene.



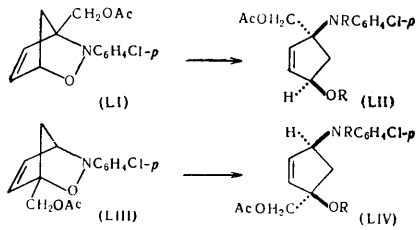
(*a*) R = CH_3, R′ = C_6H_5; (*b*) R = C_6H_5, R′ = C_6H_4Cl-*p*.

Kresze [129] investigated the structure of the addition product of *p*-chloronitrosobenzene and *trans*-1-phenylbutadiene by the method employed by Arbuzov for the adduct of nitrosobenzene and *trans*-pentadiene. The adducts (XLIII*b*) and (XLIV*b*) should yield the amino-acids (XLIX*b*) and (L*b*) respectively. In fact, on reduction of the adduct to the amino-alcohol, conversion to the diacetyl derivative, and oxidation, only the amino-acid (XLIX*b*) was isolated from the products. Hence the adduct has the structure (XLIII*b*). The nuclear magnetic resonance spectrum of the adduct confirmed the structure established by chemical means.

Kresze [129] also prepared addition products formed by *p*-chloronitrosobenzene with *trans*-1-phenylbutadienes containing methoxyl, methyl, chlorine, and a nitro-group as *para* substituent. The nuclear magnetic resonance spectra of these adducts fully corresponded with that of (XLIII*b*),

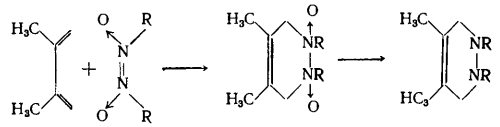
and consequently they are all 6-aryl-2-*p*-chlorophenyl--3,6-dihydro-1,2-oxazines. Thus the order of addition in the reaction of *p*-chloronitrosobenzene with *trans*-1-arylbutadienes is determined by the steric factor, not by the polarisation factor: a 1-aryl group in the diene occupies in the adduct a "*meta*" position with respect to the *p*'-chlorophenyl group.

Kresze [126] also studied the structure of the adduct from cyclopentadien-1-ylmethyl acetate and *p*-chloronitrosobenzene, which could have the structures (LI) and (LIII). Reduction of these with zinc and acetic acid should yield the compound (LII*a*) and (LIV*a*), from which the triacetyl derivatives (LII*b*) and (LIV*b*) would be formed on acetylation. Comparison of the nuclear magnetic resonance spectrum of the triacetyl derivative obtained with that of the diacetyl derivative (XXV*b*) prepared from the addition product of nitrosobenzene and cyclopentadiene showed that the proton spectrum of the former lacked a signal from the proton of a CH group linked to a nitrogen atom and to a C=C bond. Hence the triacetyl derivative had the structure (LII*b*), the adduct being (LI).



(*a*) R = H; (*b*) R = Ac.

In 1963 Hamer [120] reported that *m*- and *p*-nitronitrosobenzenes react with 2,3-dimethylbutadiene at 0° to form the normal 1 : 1 adducts and also the 2 : 1 adducts (LVI*a*) and (LVI*b*), the latter resulting from diene condensation of 2,3-dimethylbutadiene with the dimeric nitroso-compounds (LV*a*) and (LV*b*). The structure of the 2 : 1 adduct (LVI*b*) was established by reducing it with phosphorus trichloride to 1,2,3,6-tetrahydro-4,5-dimethyl-1,2-di-*p*--nitrophenylpyridazine (LVII*b*), which had been obtained in 1953 by Baranger [32] by the diene condensation of 2,3-dimethylbutadiene with *pp*'-dinitroazobenzene (see p. 410).



(*a*) R = $C_6H_4NO_2$-*m*; (*b*) R = $C_6H_4NO_2$-*p*.

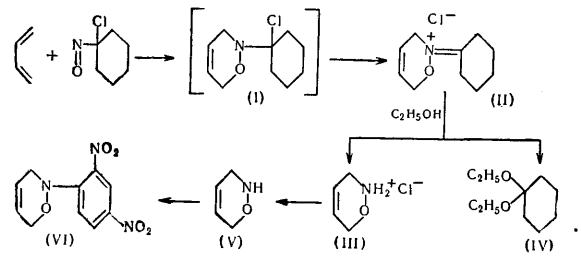
Kinetic investigation of the reaction of aromatic nitroso--compounds with 2,3-dimethylbutadiene has shown it to be of the first order with respect to each of the reactants [127].

3. Reaction of Acyclic and Alicyclic Nitroso-Compounds with 1,3-Dienes

In 1947 Wichterle [100] found that butadiene reacts in the presence of alcohol with 2-chloro-2-nitrosopropane or 1-chloro-1-nitrosocyclohexane to form a crystalline substance having the composition C_4H_8ONCl. By treating this substance with alkali he obtained a liquid C_4H_7ON, which he assumed to be 3,4-epoxypyrrolidine, while the crystalline compound was supposedly the hydrochloride of this base.

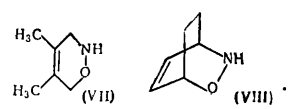
It was to be assumed that the reaction of butadiene with 1-chloro-1-nitrosocyclohexane would be one of diene synthesis, but the adduct (I) obviously underwent immediate rearrangement to the quaternary immonium salt (II), which then suffered alcoholysis to 3,6-dihydro-1,2-oxazinium chloride (III) and 1,1-diethoxycyclohexane (IV).

In order to test this hypothesis, Arbuzov and his coworkers [98,133,134] treated chloronitrosocyclohexane with butadiene in the presence of alcohol in benzene solution, and isolated the hydrochloride (III) and the ketal (IV) from the reaction mixture. If reaction was carried out at -18° in the absence of alcohol, the immonium salt (II) was obtained; this resinified rapidly on warming up to room temperature. If, however, the immonium salt was treated with alcohol cooled to -20°, the hydrochloride (III) was formed. Thus the reaction could be broken down into two stages — (1) formation of the extremely unstable immonium salt (II), and (2) alcoholysis of this salt to give the hydrochloride (III) and the ketal (IV).

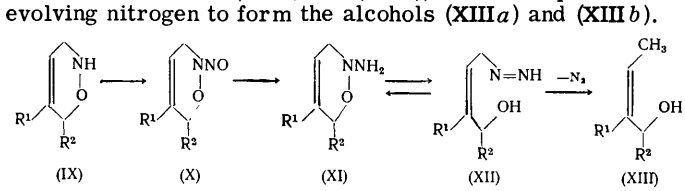


From the hydrochloride (III) was isolated the base (V), whose Raman spectrum contained the frequency of an isolated C=C bond [99]. Arylation of the base (V) with 1-chloro--2,4-dinitrobenzene gave the 2,4-dinitrophenyl derivative (VI) [133].

The action of 2,3-dimethylbutadiene and of cyclohexadiene on 1-chloro-1-nitrosocyclohexane in the presence of alcohol gave the hydrochlorides of the corresponding bases, from which the free bases (VII) and (VIII) were isolated [133].

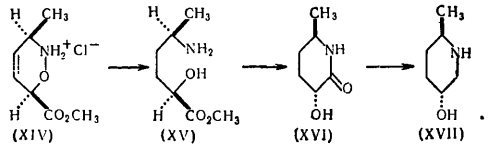


In 1950 Wichterle [135] investigated several chemical reactions of 3,6-dihydro-1,2-oxazine (V). In 1951, he showed [128] that 1-phenylbutadiene and 2-chlorobutadiene react in the presence of alcohol with 1-chloro-1-nitrosocyclohexane to form the hydrochlorides of two bases, from which the bases themselves (IX*a*) and (IX*b*) were isolated. Treatment of these bases with nitrous acid gave the *N*-nitroso-derivatives (X*a*) and (X*b*), reduction of which with zinc and acetic acid or with lithium tetrahydroaluminate yielded respectively 1-phenylbut-2-en-1-ol (XIII*a*) and 2-chlorobut-2-en-1-ol (XIII*b*). He explained the mechanism of these transformations by initial reduction of the *N*-nitroso-derivatives (X*a*) and (X*b*) to hydrazine derivatives (XI*a*) and (XI*b*), which passed into the tautomeric diimide derivatives (XII*a*) and (XII*b*), these compounds evolving nitrogen to form the alcohols (XIII*a*) and (XIII*b*).



(*a*) R^1=H, R^2=C_6H_5; (*b*) R^1=Cl, R^2=H.

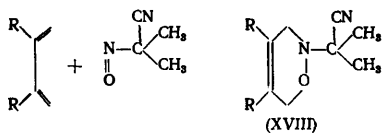
In 1963 Belleau [136] observed that 1-chloro-1-nitrosocyclohexane reacts in the presence of alcohol with methyl *trans*-*trans*-sorbate to form *cis*-3,5-dihydro-6-methoxycarbonyl-3-methyl-1,2-oxazinium chloride (XIV). The structure and the configuration of (XIV) were established by catalytic reduction to methyl *erythro*-5-amino-2-hydroxyhexanoate (XV), which on being heated to 100° gave the lactam (XVI), reduced with lithium tetrahydroaluminate to 3-hydroxy-6-methylpiperidine (XVII). This last compound was shown by its nuclear magnetic resonance spectrum to have the *trans* configuration. Consequently the ester (XV) had the *erythro* configuration, and the hydrochloride (XIV) the *cis* structure.



(XIV) (XV) (XVI) (XVII)

The hydrochloride (XIV) was used for the stereospecific synthesis of two 5-amino-5,6-dideoxy-(±)-hexanose acids.

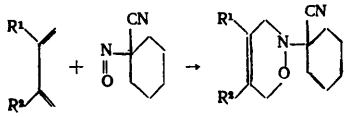
In 1957 Wichterle [137,138] showed that α-methyl-α-nitrosopropionitrile and 1-nitrosocyclohexyl cyanide react at room temperature with butadiene and 2,3-dimethylbutadiene to form the Diels–Alder adducts (XVIII*a*), (XVIII*b*), (XIX*a*), and (XIX*b*). The structure of (XVIII*a*) and (XIX*a*) was demonstrated by synthesis by Strecker's method from 3,6-dihydro-1,2-oxazine (V), a ketone (acetone or cyclohexanone), and hydrogen cyanide.



(XVIII)

(*a*) R=H; (*b*) R=CH_3.

On condensing 1-nitrosocyclohexyl cyanide with 2-chlorobutadiene, Wichterle obtained an adduct (XIX*c*) whose structure was established by synthesis from 5-chloro-3,6-dihydro-1,2-oxazine (IX*b*), cyclohexanone, and hydrogen cyanide.

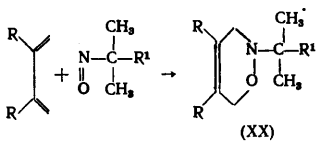


(XIX)

(*a*) $R^1=R^2=H$; (*b*) $R^1=R^2=CH_3$; (*c*) $R^1=H$, $R^2=Cl$.

According to Wichterle's results, 2-methyl-2-nitrosopropane does not react with 2,3-dimethylbutadiene. The enhanced reactivity of *gem*-chloro- and *gem*-cyano-nitroso-compounds is explained by the electron-acceptor properties of chlorine and the nitrile group, which diminished the electron density on the nitroso-group.

In 1963 Klamann [139] reported that aliphatic α-nitroso-ketones and α-nitroso-carboxylic esters, as also nitroso-alkanes containing aromatic substituents, react with 1,3-dienes to form 3,6-dihydro-1,2-oxazines (XX):



(XX)

R=H, CH_3; $R^1=COCH_3$, $CO_2C_2H_5$, C_6H_5.

Trichloronitrosomethane reacts with 1,3-dienes in the presence of alcohols to form 3,6-dihydro-1,2-oxazines and orthocarbonic esters. Aliphatic *gem*-nitro-nitroso-compounds also react with 1,3-dienes in the presence of alcohols, forming 3,6-dihydro-2-nitroso-1,2-oxazines and ketals [139].

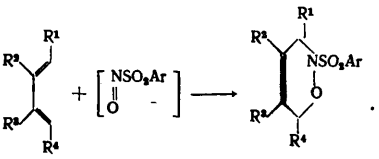
4. Reaction of 1,3-Dienes with Nitrosyl Arenesulphinates

In 1961 Kresze [140] found that aromatic sulphinic acids react with alkyl nitrites in inert solvents to form *NN*-diarenesulphonylhydroxylamines. He regarded the reaction as occurring in two stages, with the intermediate formation of nitrosyl arenesulphinate:

$$ArSO_2H+RONO \rightarrow [ArSO_2NO] + ROH,$$

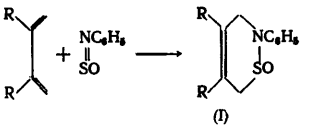
$$ArSO_2H + [ArSO_2NO] \rightarrow (ArSO_2)_2NOH.$$

To confirm this hypothesis, he carried out the reaction of aromatic sulphinic acids with ethyl nitrite in the presence of 1,3-dienes (butadiene, 2,3-dimethylbutadiene, 2-chlorobutadiene), and obtained 2-arenesulphonyl-3,6-dihydro-1,2-oxazines:



IV. DIENE SYNTHESIS WITH *N*-SULPHINYLAMINES AND *N*-SULPHINYLAMIDES

In 1953 Wichterle [141,142] showed that *N*-sulphinylaniline undergoes diene synthesis on being heated with butadiene and 2,3-dimethylbutadiene, with the formation of 3,6-dihydro-1-oxo-2-phenyl-1,2-thiazines (I*a*) and (I*b*):

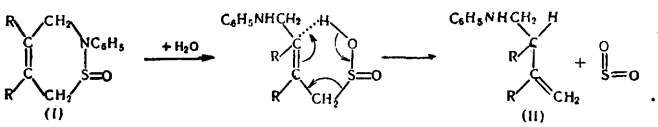


(I)

(*a*) R=H; (*b*) R=CH_3.

Other aromatic *N*-sulphinylamines have been subjected to diene synthesis. Aliphatic *N*-sulphinylamines do not react with 1,3-dienes.

The structure of the adducts (I*a*) and (I*b*) was investigated by acid hydrolysis, when the N–S bond underwent hydrolytic cleavage, sulphur dioxide was split off, and migration of the double bond occurred to give the amines (II*a*) and (II*b*). Wichterle showed that this change takes place by a cyclic mechanism.

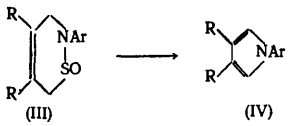


(I) (II)

(*a*) R=H; (*b*) R=CH_3.

When the adducts (III) were heated with alcoholic sodium ethoxide or caustic potash, good yields of 1-arylpyrroles

(IV) were obtained [143,144]. The mechanism of this reaction has not been elucidated.

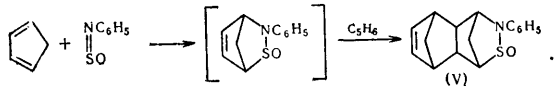


(III) (IV)

R=H, CH_3.

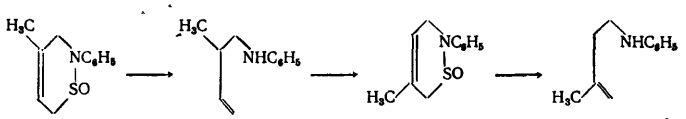
In 1962 Kataev [145] obtained addition products formed by *N*-sulphinylaniline with butadiene, isoprene, pentadiene, cyclopentadiene, and 1-*p*-nitrophenylbutadiene. Examination of the infrared spectra of *N*-sulphinylaniline and of its addition product with butadiene, as well as study of the nuclear magnetic resonance spectrum of its addition product with isoprene, confirmed the structures, established by Wichterle by chemical means, of the adducts of 1,3-dienes with *N*-sulphinylanilines.

In the reaction of *N*-sulphinylaniline with cyclopentadiene a 1:2 adduct (V) was obtained:



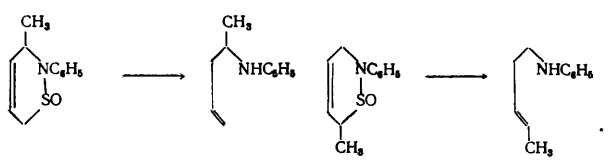
(V)

Kataev investigated the structure of the addition products formed with isoprene and pentadiene. The isoprene adduct could have the formulae (VI*a*) and (VI*b*), giving on acid hydrolysis (VII*a*) and (VII*b*). The infrared spectrum of the product showed the presence of a CH_2:CH group and the absence of CH_2:C(CH_3). Hence the adduct has the structure (VI*a*).



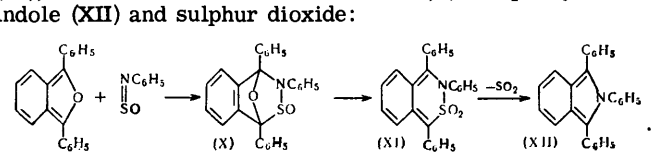
(VI*a*) (VII*a*) (VI*b*) (VII*b*)

With pentadiene the adduct could be (VIII*a*) and (VIII*b*), giving on acid hydrolysis the amines (IX*a*) and (IX*b*). The infrared spectrum of the hydrolysis product showed the presence of CH_2:CH and *trans*-CH:CH groups. Hence the Diels–Alder adduct is a mixture of the isomers (VIII*a*) and (VIII*b*).



(VIII*a*) (IX*a*) (VIII*b*) (IX*b*)

In 1963 Cava [146] discovered that *N*-sulphinylaniline reacts at elevated temperature with 1,3-diphenylisobenzofuran to form 1,2,3-triphenylisoindole (XII). He suggests a mechanism involving initial formation of the Diels–Alder adduct (X), which rearranges to the *o*-quinonoid δ-sultam (XI), and the latter breaks down into 1,2,3-triphenylisoindole (XII) and sulphur dioxide:



(X) (XI) (XII)

In 1962 Kirsanov and his coworkers [147,148] found that *N*-sulphinylarenesulphonamides react at room temperature with butadiene and 2,3-dimethylbutadiene to form 2-arenesulphonyl-3,6-dihydro-1-oxo-1,2-thiazines (XIII*a*) and (XIII*b*):

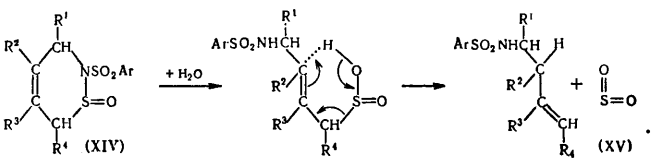
(XIII)

(*a*) R=H; (*b*) R=CH_3.

N-Sulphinylarenesulphonamides take part considerably more readily in diene synthesis than do the structurally similar *N*-sulphinylanilines. The explanation is that replacement of the aryl group of the latter by the more strongly electron-accepting arenesulphonyl group results in a greater decrease in electron density on the sulphinyl group.

Kresze [149,150] obtained addition products from *N*-sulphinylarenesulphonamides with butadiene, 2,3-dimethylbutadiene, 2-chlorobutadiene, cyclohexadiene, 2-chlorocyclohexadiene, 1-*p*-nitrophenylbutadiene, and ethyl sorbate.

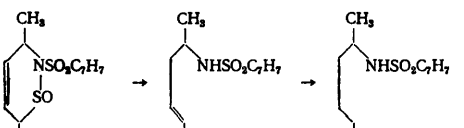
Studies of the chemical properties of the adducts made by Kresze and by Kirsanov showed them to differ in many respects from the properties of 2-aryl-3,6-dihydro-1-oxo-1,2-thiazines. In both acid and alkaline hydrolysis of the adducts (XIV) the ring underwent hydrolytic cleavage at the N–S bond, sulphur dioxide was eliminated, and sulphonamides (XV) were formed with migration of the double bond:



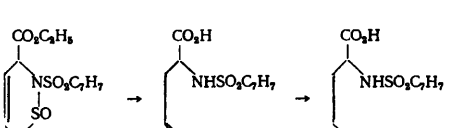
(XIV) (XV)

In no case could pyrrole derivatives be isolated from the products of alkaline hydrolysis of the adducts.

In order to ascertain the order in which *N*-sulphinylarenesulphonamides add on to unsymmetrical dienes, Kresze [149] investigated the structure of the addition products formed by *N*-sulphinyltoluene-*p*-sulphonamide with ethyl sorbate and with 1-*p*-nitrophenylbutadiene. The adduct obtained with ethyl sorbate could have the structure (XVI*a*) or (XVI*b*), which on hydrolysis would give an *N*-toluene-*p*-sulphonyl derivative of an unsaturated amino-acid (XVII*a*) or (XVII*b*), and this could be reduced to the corresponding derivative (XVIII*a*) or (XVIII*b*) of aminohexanoic acid. Examination of the product showed it to have the structure (XVIII*a*), and hence the adduct was (XVI*a*).

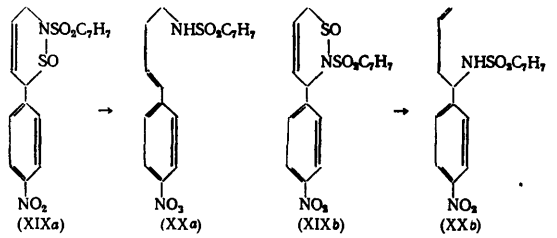


(XVI*a*) (XVII*a*) (XVIII*a*)



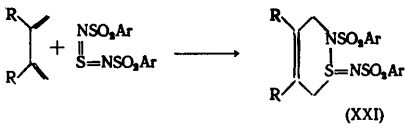
(XVI*b*) (XVII*b*) (XVIII*b*)

1-*p*-Nitrophenylbutadiene could give the adducts (XIX*a*) and (XIX*b*), which on hydrolysis should form the sulphonamides (XX*a*) and (XX*b*). The infrared spectrum of the hydrolysis product showed the absence of a CH_2 : CH group and the presence of a *trans*-CH : CH group, while the ultraviolet spectrum showed a *p*-nitrostyrene residue to be present. Hence the adduct has the structure (XIX*a*).



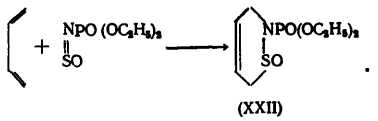
Kresze considers that in both the cases investigated the order of addition is determined mainly by the steric factor: a bulky substituent present in position 1 in the diene is oriented "*meta*" to the arenesulphonyl group in the adduct.

In 1962 Kirsanov [151] observed that sulphur di-*N*-arenesulphonylimides react readily with butadiene and 2,3-dimethylbutadiene to form 2-arenesulphonyl-1-arenesulphonylimino-3,6-dihydro-1,2-thiazines (XXI*a*) and (XXI*b*):



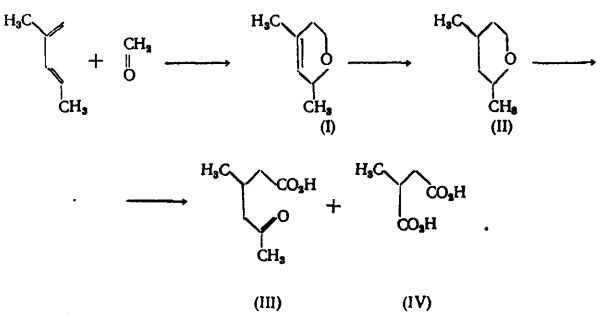
(*a*) R=H; (*b*) R=CH_3.

In 1963 Wieczorkowski [152] reported that diethyl *N*-sulphinylphosphoramidate reacts with butadiene to form 2-diethoxyphosphinyl-3,6-dihydro-1-oxo-1,2-thiazine (XXII):

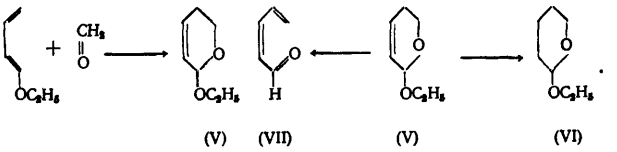


V. DIENE SYNTHESIS WITH CARBONYL AND THIOCARBONYL COMPOUNDS

In 1949 Gresham and Steadman [153] showed that 2-methylpentadiene reacts at 185° with paraformaldehyde to produce Δ^3-dihydro-2,4-dimethylpyran (I). Catalytic reduction of the adduct gave tetrahydro-2,4-dimethylpyran (II), oxidation of which with chromic acid mixture yielded 3-methyl-5-oxohexanoic acid (III) and methylsuccinic acid (IV).

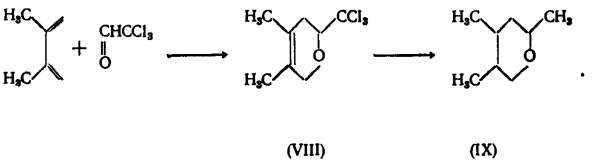


In 1959 Kubler [154,155] treated 1-ethoxybutadiene with paraformaldehyde at 180°, and obtained 2-ethoxy-Δ^3-dihydropyran (V), which was converted by catalytic reduction into 2-ethoxytetrahydropyran (VI) and by acid hydrolysis into pentadienal (VII).

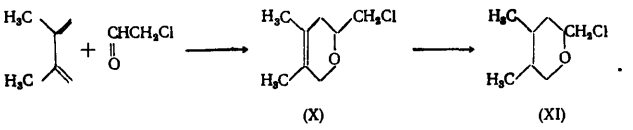


Diene adducts were obtained also from paraformaldehyde with 1-methoxybutadiene, 1-2′-methoxyethoxybutadiene, 1-2′-ethylhexyloxybutadiene, 1-methoxyhexadiene, and 2-ethyl-1-methoxybutadiene.

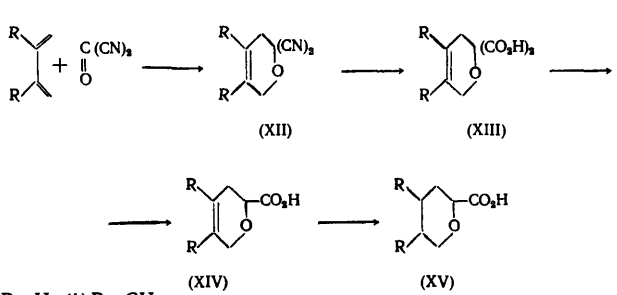
In 1954 Dale and Sisty [156] obtained the diene adduct (VIII) by heating chloral with 2,3-dimethylbutadiene at 150°. Catalytic reduction of the adduct gave a tetrahydropyran derivative (IX).



Isoprene and pentadiene also reacted at 150° with chloral to form diene adducts. Later these workers showed [157] that chloroacetaldehyde reacted at 100° with 2,3-dimethylbutadiene to form the adduct (X), which was catalytically reduced to the tetrahydropyran derivative (XI):

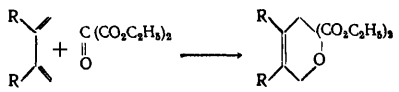


In 1957 Achmatowicz [158-160] investigated the reaction of carbonyl cyanide [mesoxalonitrile] with butadiene and 2,3-dimethylbutadiene. In both cases diene condensation occurred even at room temperature to give the adducts (XII*a*) and (XII*b*). The structure of (XII*a*) was established by alkaline hydrolysis to the dicarboxylic acid (XIII*a*), which was readily decarboxylated to the monocarboxylic acid (XIV*a*), catalytic hydrogenation of which gave the known tetrahydropyran-2-carboxylic acid (XV*a*). In a similar manner the acid (XV*b*) was obtained from the adduct (XII*b*).



(*a*) R=H; (*b*) R=CH_3.

Achmatowicz established [158-160] that diethyl mesoxalate condenses with butadiene at 135° and with 2,3-dimethylbutadiene at 70° to give the adducts (XVI*a*) and (XVI*b*):

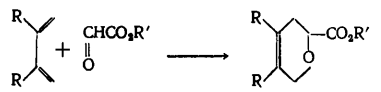


(XVI)

(*a*) R=H; (*b*) R=CH_3.

He also obtained adducts from diethyl mesoxalate with isoprene, pentadiene, hexa-2,4-diene, cyclohexadiene, and ethyl sorbate [160].

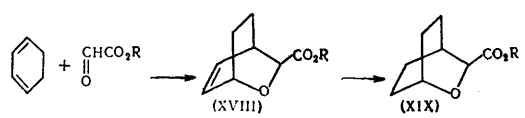
In 1962 Arbuzov *et al.* [161] showed that butadiene and 2,3-dimethylbutadiene react at 120–130° with ethyl glyoxylate, n-butyl glyoxylate, or their hemiacetals to form the Diels–Alder adducts (XVII*a*) and (XVII*b*):



(XVII)

(*a*) R=H, R′=C_2H_5, n-C_4H_9; (*b*) R=CH_3, R′=C_2H_5, n-C_4H_9.

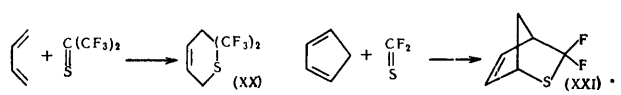
Cyclohexadiene with n-butyl glyoxylate gave the adduct (XVIII), which was reduced to the tetrahydropyran derivative (XIX):



(XVIII) (XIX)

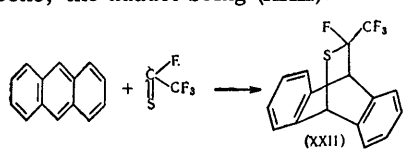
R=n-C_4H_9.

In 1961 Middleton *et al.* [162] discovered that several thiocarbonyl compounds readily undergo diene synthesis. Hexafluorothioacetone reacts instantaneously with butadiene at -78° to give the theoretical yield of the adduct (XX). Thiocarbonyl fluoride reacts rapidly at -20° with cyclopentadiene to form the adduct (XXI).



(XX) (XXI).

Trifluorothioacetyl fluoride reacts at room temperature with anthracene, the adduct being (XXII):



(XXII).

VI. DIENE SYNTHESIS WITH NITRILES

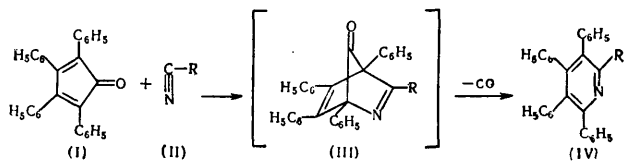
1. Reaction of Aromatic Nitriles with Cyclones

In 1935 Dilthey [163] found that tetracyclone (I) reacts with benzonitrile (II*a*) at 275–300° to form pentaphenylpyridine (IV*a*). An unstable Diels–Alder adduct containing an *endo*-carbonyl bridge (III*a*) is probably formed initially, and breaks down under the experimental conditions into carbon monoxide and (IV*a*).

In 1952 Polaczkowa and Woliński [164] showed that tetracyclone (I) condenses at 230–280° with *p*-tolunitrile (II*b*), *p*-methoxybenzonitrile (II*c*), and *p*-bromobenzonitrile (II*d*) to form the corresponding pentaarylpyridines (IV*b*–*d*).

In 1960 Jaworski [165] established that tetracyclone (I) reacts at 215° with 2-, 3-, and 4-cyanopyridines (II*e*–*g*) with the formation of 3,4,5,6-tetraphenyl-2,2′(3′ and 4′)-bipyridyls (IV*e*–*g*).

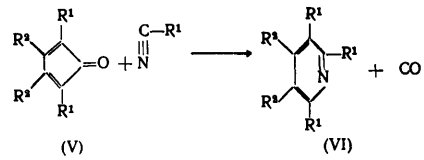
Polaczkowa *et al.* [166] condensed tetracyclone (I) with benzoyl cyanide (II*h*) and with *p*-methoxybenzoyl cyanide (II*i*) at 235°, and obtained the tetraphenylpyridine derivatives (IV*h*) and (IV*i*).



(I) (II) (III) (IV)

R = (*a*) phenyl, (*b*) *p*-tolyl, (*c*) *p*-methoxyphenyl, (*d*) *p*-bromophenyl, (*e*) pyrid-2-yl, (*f*) pyrid-3-yl, (*g*) pyrid-4-yl, (*h*) benzoyl, (*i*) *p*-methoxybenzoyl.

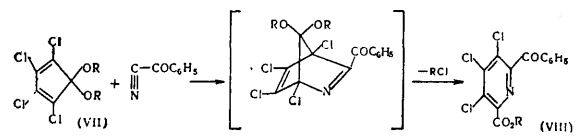
Madroñero Peláez [167] found that heating anisylcyclone (V) with benzonitrile gives the pentaarylpyridine (VI) and carbon monoxide:



(V) (VI)

R^1=phenyl; R^2=*p*-anisyl.

In 1960 Jaworski and Polaczkowa [168] reported that heating the 5,5-dialkoxytetrachlorocyclopentadienes (VII*a*) and (VII*b*) with benzoyl cyanide gives the 6-benzoyl-3,4,5-trichloropyridine-1-carboxylic esters (VIII*a*) and (VIII*b*)†:



(VII) (VIII)

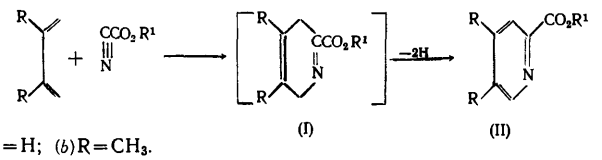
(*a*) R=CH_3; (*b*) R=C_2H_5.

Jaworski [170,171] investigated the kinetics of the reaction of tetracyclone with 2-cyanopyridine, *o*-chlorobenzonitrile, and benzonitrile, and found it to be overall of the second order.

† It has recently been found [169] that the ketal (VII*a*) condenses with dimethyl acetylenedicarboxylate to form trimethyl hemimellitate and methyl chloride.

2. Reaction of Nitriles with 1,3-Dienes

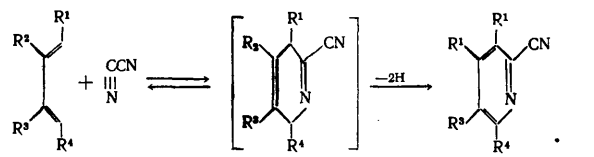
In 1943 Alder [172] reported that butadiene and 2,3-dimethylbutadiene undergo diene synthesis with cyanoformic esters to give the 2,5-dihydropyridine derivatives (I*a*) and (I*b*), which under the experimental conditions are dehydrogenated to the pyridine derivatives (II*a*) and (II*b*):



(I) (II)

(*a*) R=H; (*b*) R=CH_3.

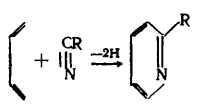
During 1947–1949 Janz [173-178] published a series of papers in which he showed that cyanogen reacts in the vapour phase at 400–600° with 1,3-dienes (butadiene, isoprene, 2-methylpentadiene, and 2-chlorobutadiene) with the formation of 2-cyanopyridines. In this reaction unstable Diels–Alder adducts, 2-cyano-3,6-dihydropyridines (III), are probably formed initially, and break down under the conditions of the experiment into hydrogen and 2-cyanopyridines (IV):



(III) (IV)

Condensation of cyanogen with butadiene at 480°, for example, gave an 18% yield of 2-cyanopyridine (V*a*). [178] 2,2′-Bipyridyl, a condensation product of 2-cyanopyridine with butadiene, was also isolated from the reaction mixture. A kinetic investigation of the reaction between cyanogen and butadiene showed it to be overall of the second order, and of the first order with respect to each of the reactants [179].

Janz [177] found that butadiene reacts at 400–600° with hydrogen cyanide, acetonitrile, and benzonitrile to form respectively pyridine (V*b*), 2-methylpyridine (V*c*), and 2-phenylpyridine (V*d*). Marvel [180] obtained 2-ethylpyridine (V*e*) by the condensation of butadiene with propionitrile at 600°.



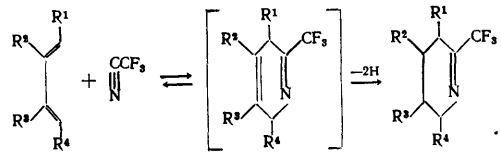
(V)

(*a*) R=CN; (*b*) R=H; (*c*) R=CH_3; (*d*) R=C_6H_5; (*e*) R=C_2H_5; (*f*) R=C_2H_3.

Janz and his coworkers [181-188] found that the condensation of 1,3-dienes with nitriles is catalysed by metal oxides. Reaction of butadiene with cyanogen, hydrogen cyanide, acetonitrile, benzonitrile, propionitrile, and acrylonitrile at 400° in the presence of chromic oxide or activated aluminium oxide gave respectively the pyridines (V*a–f*).

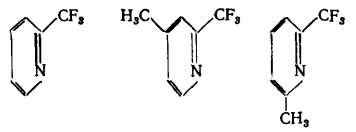
Catalytic condensation of acetonitrile and benzonitrile with isoprene, pentadiene, 2-methylpentadiene, and 2,3-dimethylpentadiene at 400° in the presence of activated aluminium oxide gave the corresponding pyridine derivatives.

It was found in 1956 [189,190] that trifluoroacetonitrile reacts in the gas phase with 1,3-dienes to form 2-trifluoromethylpyridines (VI):



(VI)

Condensation of trifluoroacetonitrile with butadiene, isoprene, and pentadiene at 400° gave high yields of 2-trifluoromethylpyridine (VII), 4-methyl-2-trifluoromethylpyridine (VIII), and 2-methyl-6-trifluoromethylpyridine (IX) respectively.



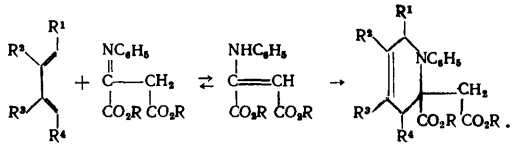
(VII) (VIII) (IX)

Kinetic investigation of the reaction between butadiene and trifluoroacetonitrile showed it to be overall of the second order, and of the first order with respect to each reactant [191].

The high reactivity of trifluoroacetonitrile in diene synthesis is explained by the strong electrophilic properties of the trifluoromethyl group, which results in a decrease in the electron density on the nitrile group.

VII. DIENE SYNTHESIS WITH AZOMETHINES

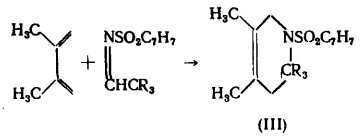
In 1943 Alder [172] reported that the anil of oxaloacetic ester (I*a*), a tautomer of anilinomaleic ester (I*b*), enters into diene synthesis with 1,3-dienes to give 1,2,3,6-tetrahydropyridine derivatives (II):



(I*a*) (I*b*) (II)

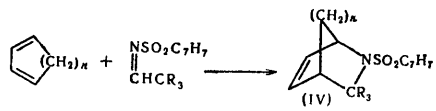
In 1964 Kresze [192] showed that the *N*-toluene-*p*-sulphonylimines of chloral and fluoral react in boiling benzene with 1,3-dienes to form 1,4 adducts which are 1,2,3,6-tetrahydropyridine derivatives. High (93–96%) yields were obtained of the addition products (III*a*) and (III*b*) formed by *N*-trichloroethylidene- and *N*-trifluoroethylidene-toluene-*p*-sulphonamides with 2,3-dimethylbutadiene, the addition

product (IV*a*) of the former sulphonamide with cyclopentadiene, and the addition product (IV*b*) of the latter sulphonamide with cyclohexadiene.



(III)

(*a*) R = Cl; (*b*) R = F.



(IV)

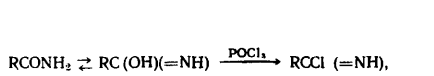
(*a*) *n* = 1, R = Cl; (*b*) *n* = 2, R = F.

Examination of the infrared spectra of the addition products showed them to be 1,4 adducts. The addition product (IV*a*) gave an adduct with phenyl azide.

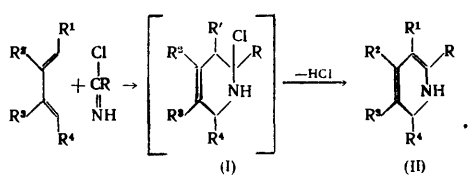
The ability of the *N*-arenesulphonylimines of chloral and fluoral to take part in diene synthesis is explained by the strong electrophilic properties of arenesulphonyl and trihalogenomethyl groups, which result in a decrease in electron density on the azomethine group.

VIII. DIENE SYNTHESIS WITH IMIDOYL CHLORIDES

In 1958 Lora-Tamayo [193,194] found that 1,3-dienes react with alkanoamides or aldoximes in the presence of phosphoryl chloride to give 1,2-dihydropyridine derivatives. Reaction was carried out either in nitrobenzene at 170–180° or in benzene or toluene at 120–130°. It was suggested that the amides or aldoximes were first converted by the phosphoryl chloride into imidoyl chlorides:

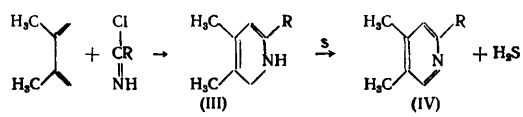


The imidoyl chlorides then underwent diene synthesis with the 1,3-dienes to form adducts (I), which decomposed under the experimental conditions into hydrogen chloride and 1,2-dihydropyridines (II):



(I) (II)

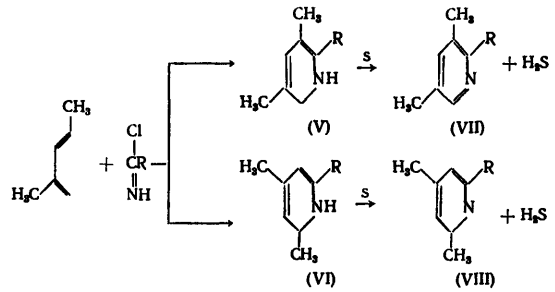
By this method the 1,2-dihydropyridine derivatives (III*a–c*) were obtained from 2,3-dimethylbutadiene with formamide, acetamide (or acetaldoxime), and benzamide (or benzaldoxime):



(III) (IV)

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

From 2-methylpentadiene with formamide and acetamide were obtained mixtures respectively of the isomers (V*a*) and (VI*a*) and of (V*b*) and (VI*b*):



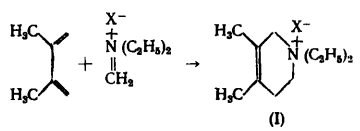
(V) (VII) (VI) (VIII)

(*a*) R = H; (*b*) R = CH_3.

Heating the dihydropyridines (III*a*), (III*b*), (V*a*), and (VI*a*) with sulphur yielded the pyridines (IV*a*), (IV*b*), (VII*a*), and (VIII*a*).

IX. DIENE SYNTHESIS WITH QUATERNARY IMMONIUM SALTS

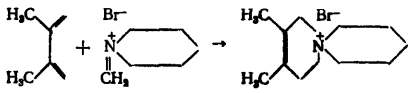
In 1963 Böhme [195] established that 2,3-dimethylbutadiene reacts in dichloromethane with quaternary immonium salts by a mechanism of diene synthesis to form quaternary 1,2,3,6-tetrahydropyridinium salts. Methylenediethylammonium chloride and bromide react with 2,3-dimethylbutadiene at room temperature to give the adducts (I*a*) and (I*b*):



(I)

(*a*) X = Cl; (*b*) X = Br.

N-Methylenepiperidinium bromide condenses with 2,3-dimethylbutadiene at 40° to form the adduct (II):



(II)

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PROGRESS IN THE CHEMISTRY OF THE AMINODEOXY-SUGARS

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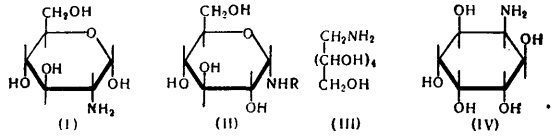
I. INTRODUCTION

Aminodeoxy-sugars or glycosamines (I) [subsequently abbreviated to AS in the Russian text; this nomenclature has not been retained here (Ed. of Translation)] are carbohydrates containing amino-groups in place of alcoholic hydroxyl groups, and differ from *N*-glycosides (glycosylamines) (II), in the molecules of which the amino-group takes the place of a hemiacetal hydroxyl. A characteristic difference between aminodeoxy-sugars and *N*-glycosides is generally the stability of the carbon–nitrogen bond in the former and the lability of this bond in the latter[1-3]. Aminodeoxy-sugars are sometimes called "amino-sugars", but this term is not sufficiently unambiguous.

Compounds genetically related to the aminodeoxy--sugars are their reduction products — acyclic polyhydric alcohols containing amino-groups — the aminodeoxy-sugar alcohols† (III). Finally, compounds similar to the aminodeoxy-sugars and aminodeoxy-sugar alcohols are the aminodeoxy-derivatives of cyclic alcohols, *i.e.* polyhydroxycyclohexanes, called inosamines[5,6] (IV):



For a long time only two aminodeoxy-sugars — both of natural origin — were known: 2-amino-2-deoxy-D-glucose (glucosamine, 1878) and 2-amino-2-deoxy-D-galactose (galactosamine, 1914), whose configuration was established only in 1937–1939 [7] and 1945 [8] respectively. Individual synthetic aminodeoxy-sugars and aminodeoxy--sugar alcohols were prepared by Fischer and coworkers[9,10], Freudenberg, Helferich, Ohle, and others. Particular interest in aminodeoxy-sugars was aroused by the discovery of 2-deoxy-2-(*N*-methylamino)-L-glucose in the products arising from the extensive degradation of the antibiotic streptomycin[11]; later, other amino-sugars were found in a number of antibiotics. Individual inosamines were also found as components of antibiotics[5]. At the same time increasing attention was drawn to the discovery of aminodeoxy-sugars in biologically important polysaccharides and proteins. In this connection a large number of papers have been published in the last 15 years on the improvement of old methods and the development of new methods for the synthesis of aminodeoxy-sugars and aminodeoxy-sugar alcohols and the study of their properties, and also on the determination of the structure of a number of aminodeoxy-sugars of natural origin.

The importance of aminodeoxy-sugars at the present time is due to the fact that they are present in important macromolecular substances which are found in living organisms and in a number of cases exhibit biological activity; they also take part in the exchange of matter. They

† Aminodeoxy-sugar alcohols with an amino-group on a primary carbon atom are usually called glycamines[1]; it has been suggested[4] that this term be used for aminodeoxy-sugar alcohols in general.

arepresent in bacterial organisms, crabs' shells, insects, fungi, and soil compounds. Aminodeoxy-sugars are components of a number of antibiotics and oligosaccharides of human milk. Work is being carried out on the use of aminodeoxy-sugars and aminodeoxy-sugar alcohols as drugs, surface-active agents, and starting materials for the preparation of polymers, etc.

A number of reviews[2,12-18] and reference tables[19] devoted partly or entirely to aminodeoxy-sugars have been published; the paper by Foster and Horton[18] is particularly noteworthy‡. In the present review an attempt is made to describe the present state of this field. We have considered it advisable to restrict ourselves to the amino--derivatives of simple sugars. The volume and importance of the chemistry of the amino-polysaccharides are such that this subject requires separate treatment (see other reviews[17,18,20-24]).

II. SYNTHESIS OF AMINODEOXY-SUGARS AND AMINODEOXY-SUGAR ALCOHOLS

The methods for the synthesis of aminodeoxy-sugar and aminodeoxy-sugar alcohols can be divided into three groups: (1) the direct introduction of an amino-group into a sugar; this includes the specific methods for preparing 2-amino--2-deoxyaldoses and 1-amino-1-deoxyketoses; (2) the introduction of nitrogen-containing groups into a sugar and conversion of the former into amino-groups; (3) the conversion of aminodeoxy-sugars into other aminodeoxy--sugars and aminodeoxy-sugar alcohols. These methods are considered below in the order listed.

1. Direct Introduction of an Amino-Group into a Sugar

(a) Introduction of an amino-group by substitution. The most widely used method involves the introduction of amino-groups into the molecules of sugars (or sugar alcohols) by the action of ammonia (or amines) on the readily accessible sugar sulphonates (V)[25] according to the scheme:

$$\underset{(V)}{\text{Sug-OSO}_2\text{R}} + \text{NH}_3 \text{ (or NHR'R'')} \rightarrow \text{Sug-NH}_2 \text{ (or Sug-NR'R'')},$$

where R, R', and R'' are alkyl or aryl groups and Sug the residue formed by removing OH from the molecule of a monosaccharide or polyhydric alcohol.

The reaction takes place with varying ease, depending on the position of the group being replaced in the sugar molecule, the structure of the sugar, and the nature of the amine used. No differences were observed in the reactions of ammonia with a number of esters (the 3-*p*-toluene-, 3-ethane-, and 3-naphthalene-sulphonates of 1,2:5,6-di-*O*--isopropylidene-D-glucose[26]). In the case of the *p*-nitrobenzenesulphonates, however, solvolysis takes place instead of substitution[27].

The opinion exists that benzenesulphonates react with amines more readily than *p*-toluenesulphonates[28,29]. Although substitution at a secondary carbon atom is much more difficult than substitution at a primary carbon atom, cases of the direct formation of the corresponding amino--derivatives have been described: 3,5-methylene-2-*p*--toluenesulphonyl-1,4-xylitan reacts in good yield with butylamine at 120° and with aniline at 140°.[30]§

Substitution is also comparatively difficult in the 1-position in ketoses[26], but this is unimportant, since the corresponding amino-derivatives are more conveniently prepared by the Amadori rearrangement (see below).

The reaction rate evidently depends to a marked extent on steric factors: 1,5-di-*O*-benzenesulphonyl-D-mannitol reacts with aniline at 25°, whereas the corresponding 2,4:3,5-dimethylene derivative reacts only after boiling for 42 h in dioxan[28]. The replacement of the corresponding residues by amino-groups should apparently take place more readily in the case of compounds with an open chain (aminodeoxy-sugar alcohols or sugar thioacetals) than in the case of aminodeoxy-sugars; this was shown by the action of sodium iodide[31].

Substitution with the formation of aminodeoxy-sugars and aminodeoxy-sugar alcohols can generally be carried out only when the neighbouring hydroxyl groups are blocked with substituents which are not removed during amination. If this is not the case, the products are anhydro-compounds, which may undergo further changes[25]. 1,4-Anhydro--5-chloroxylitol, however, reacts smoothly with aqueous ammonia and a number of amines to give the 5-amino--derivatives of 1,4-anhydroxylitol[32]. Similarly, methyl 6-*p*-toluenesulphonyl-α-D-glucoside reacts with ammonia in methanol to form methyl 6-amino-6-deoxy-α-D-glucoside[33]. At the same time the analogous galactoside gives not the amino-sugar but the anhydrogalactoside[34].

The reaction of the sulphonates with amines and other nucleophilic reagents takes place with Walden inversion by an S_N2 mechanism[35]. This is confirmed by kinetic data: the reaction takes place according to a second-order equation and its rate is proportional to the nucleophilic power of the reagent[36]. The configuration of some previously--prepared aminodeoxy-sugars[37,38] were corrected on the basis of data obtained by Cope and Shen[35].

The significance of the nature of the amine was illustrated by the reaction of 1,2:3,4-di-*O*-isopropylidene-6--*p*-toluenesulphonyl-D-galactose with 16 different aromatic amines in butanol at 100°. The reaction rate was found to be greater, the greater the basic strength of the amine used: the yields of aminodeoxy-sugars were high in the case of anisidines, toluidines, and aniline, whereas in the case of nitroanilines, dichloroaniline and other weakly--basic amines, the reaction took place extremely slowly[36].

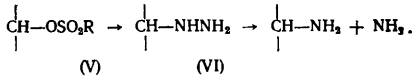
Glycoseens and secondary and tertiary amines[25,39] of the type $(\text{Sug})_2\text{NH}$ and $(\text{Sug})_3\text{N}$ are formed in side reactions. Unexpectedly, 6-iodo-1,2:3,4-di-*O*-isopropylidene-D-galactose reacted with ammonia in methanol to give the 6-methylamino-derivative of galactose, as a result of the reaction between the initially-formed aminodeoxy-sugar and the methyl iodide produced during the reaction[39].

The sulphonates react much more readily with liquid hydrazine than with ammonia solutions. Thus a method has been proposed for the synthesis of aminodeoxy-sugars (particularly those with an amino-group on a secondary

‡ *Note added in proof*. A number of additional reviews have recently been published[282-284].

§ *Note added in proof*. The methanesulphonyl group is readily replaced in 4-*O*-benzoyl-1,2:5,6-di-*O*-isopropylidene-3-*O*--methanesulphonyl-D-mannitol[285].

carbon atom) by the hydrogenolysis of the hydrazine-derivatives (VI); this method avoids the difficulties associated with direct treatment with ammonia[40]:



(V) (VI)

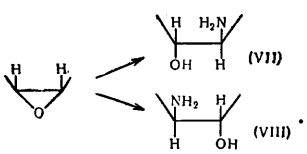
The reaction of sugar sulphonates with hydrazine at 150°, however, is accompanied by a large number of side reactions involving the formation of symmetrical and unsymmetrical disubstituted hydrazines, tri-substituted hydrazines, and reduction products — deoxymonosaccharides and thiols[41]. Steric factors are important: hydrazine reacts with the α-anomer, but not the β-anomer, of methyl 3,5-*O*-isopropylidene-2-*p*-toluenesulphonyl-L-xyloside[42].

The action of guanidine in methanol at 100° and 140° did not lead to the introduction of the guanidino-group into 1,2:5,6-di-*O*-isopropylidene-3-*p*-toluenesulphonyl-D-glucofuranose or 1,2:3,4-di-*O*-isopropylidene-6-*p*-toluenesulphonyl-D-galactopyranose; instead, solvolysis of the sulphonyl group took place[43,44].

Use is also made of the oldest method[10] in which an amino-group replaces a halogen atom in halogen-derivatives of sugars and sugar alcohols, particularly for the preparation of aminodeoxy-sugar alcohols[30,32,45]. The secondary amine was not formed by the action of ammonia on 1-chlorodimethylenexylitol, but was formed with the corresponding sulphonate[30].

A method for preparing halogeno-derivatives by the action of halogen-containing complexes of triphenyl phosphite on the sugar has been developed; in individual cases, migration of the alkylidene protection is observed[46]. A method for the introduction of halogen by the action of alkyl halides on the phosphinites of sugar alcohols has been proposed[47].

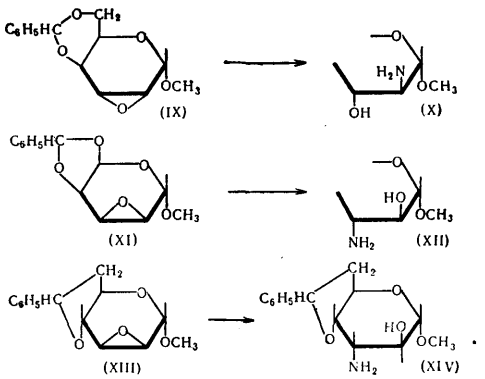
(b). The addition of ammonia and amines to sugar oxides is widely used in the synthesis of aminodeoxy-sugars[48,49]. When the oxide ring is split in this reaction, the resulting hydroxyl and amino-groups occupy the *trans*-position and the process in general takes place in two directions with the formation of the two possible isomeric aminodeoxy-sugars (VII) and (VIII):



(VII) (VIII)

In the case of the 5,6-anhydrides of hexofuranoses, only the 6-amino-derivatives are obtained[50,51]. In other cases the yield of isomers depends on the structure of the anhydride molecule and in particular on the pressure of additional rings. For example, ammonolysis of methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-guloside (IX) gave only the 2-amino-2-deoxy-D-idose derivative (X) and the corresponding taloside (XI) gave the 3-amino-3-deoxy-D-idose derivative (XII).[52]

The 2,3-anhydromannoside (XIII) gives only the 3-amino-3-deoxy-D-altroside (XIV).[53] The ring opens with the production of groups in the axial position.

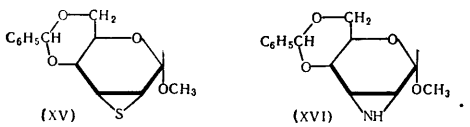


(IX) (X) (XI) (XII) (XIII) (XIV)

It has been proposed that the disulphonates be used directly instead of the anhydrides and that the ammonolysis be carried out in the presence of sodium methoxide: in this case the α-anhydride is first formed and immediately adds on ammonia. Thus methyl 4,6-*o*-benzylidene-2,3-di-*O*-toluenesulphonyl-α-D-galactopyranoside gave the corresponding derivative of 2-amino-2-deoxy-D-idose and 3-amino-3-deoxy-D-idose in 46% and 26% yields respectively[54].

The addition of ammonia to α-oxides is often used for the preparation of aminodeoxy-sugars with an amino-group on a secondary carbon atom. It has been noted that the use of the 5,6-anhydrides for the preparation of 6-aminohexoses is less suitable than direct replacement of sulphonyl groups[55].

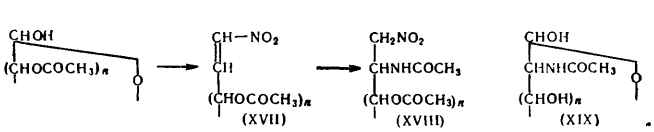
An attempt to use the corresponding thio-analogue (episulphide) instead of the α-anhydrides for the preparation of sulphur-containing aminodeoxy-sugars did not give satisfactory results: methyl 2,3-epithio-α-D-allopyranoside (XV) reacts with ammonia only at 100°, with the formation of a polymer[56]. The α-ethylenimine (XVI) has been obtained as a possible starting material in the synthesis of aminodeoxy-sugars[57].



(XV) (XVI)

Instead of the α-oxides, it is possible to use the β-oxides, which, as shown for the case of dianhydroxylitol, can be split by ammonia or amines at 140° to give the corresponding aminodeoxy-sugar alcohols[58].

(c). The addition of ammonia to unsaturated derivatives of sugars. The condensation of nitromethane with acetylated aldoses according to the usual scheme gives 1-nitro-substituted unsaturated alcohols (XVII) which can add on ammonia across the double bond with the formation of nitroacetamido-polyhydric alcohols (XVIII):



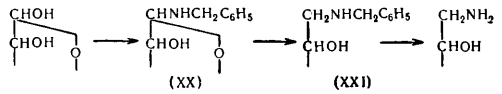
(XVII) (XVIII) (XIX)

The latter are converted into the sodium derivative and then treated with sulphuric acid to remove the nitro-group and give the acetylated aminodeoxy-sugars (XIX): usually,

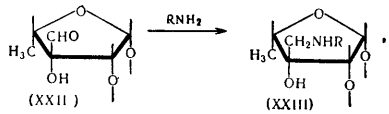
one epimer is obtained. By these reaction, D- and L--arabinose gave D- and L-mannosamine respectively[59] and D-xylose gave D-gulosamine, identical with the natural product obtained from the degradation of the antibiotic streptothricin[60].

An interesting paper by Paulsen[61] describes the preparation of derivatives of 5-amino-5-deoxyaldoses *via* unsaturated nitro-compounds.

(d). The reductive amination of aldoses and derivatives of aldonic acids with ammonia or amines in the presence of hydrogenating catalysts leads to the formation of aminodeoxy-sugar alcohols[62]. The best yields are obtained by starting from *N*-benzylglycosylamines (XX)[63]; the *N*-benzylglycamines (XXI) are formed initially and converted into aminodeoxy-sugar alcohols by hydrogenolysis.



Aminodeoxy-sugars can be obtained in this way from the ω-formyl derivatives of aldoses. This reaction has been carried out with streptomycin, whose component streptose (3-*C*-formyl-1-lyxomethylose) (XXII) is converted into an aminodeoxy-sugar residue (XXIII) according to the scheme:

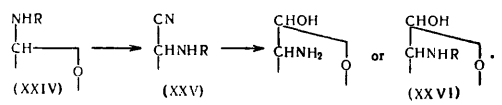


where R = H, C_8H_{17}, C_9H_{19}, $C_{12}H_{25}$, $C_{14}H_{29}$, or $C_{16}H_{33}$. The resulting *N*-alkyl-streptomycins exhibit antibacterial activity[64].

Reduction of the amide of alginic acid gives a polysaccharide with CH_2NH_2 groups[65].

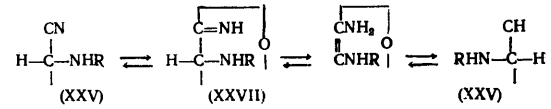
2. Methods for the Synthesis of 2-Amino-2-deoxyaldoses and 1-Amino-1-deoxyketoses

(a). The aminonitrile synthesis. The ordinary aminonitrile synthesis, used at an early date by Fischer[9] for the synthesis of glucosamine, was transformed by Kuhn and coworkers into an extremely fruitful method which has been used for the preparation of a number of 2-amino-2-deoxyaldoses[66]. The starting materials are the *N*-glycosides of the aldoses (XXIV), which with hydrogen cyanide give the aminonitriles (XXV); the latter undergo partial hydrogenation and hydrolysis:

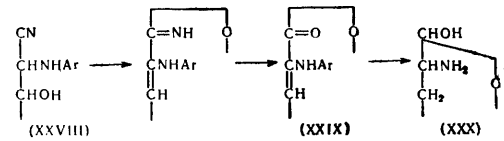


The benzyl or aryl aglycones (or the fluorene residue[67]) are split off under the conditions of the hydrogenation and give aminodeoxy-sugars with a primary amino-group; *N*-alkyl glycosides give *N*-alkyl-substituted aminodeoxy--sugars (XXVI, R = alkyl).

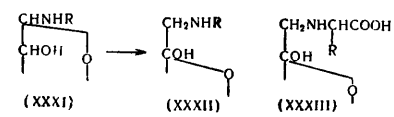
The mixture of epimeric aminodeoxy-sugars formed in this synthesis contains chiefly the epimer with the amino--group in the *trans*-position relative to a hydroxyl group on a neighbouring carbon atom. A method of directed epimerisation has been found; for example, the nitriles of *N*-benzylmannosaminic and *N*-benzylglucosaminic acids (from benzylarabinosylamine), when heated in dilute alcoholic solution, from equilibrium mixtures (~1:1) from which the first nitrile is separated by the addition of petrol. Hydrogenation of this compound gives mannosamine in 40% yield, calculated on the original arabinose[69]. D-Talosamine and D-allosamine were prepared in analogous fashion[67]. Epimerisation of the aminonitrile (XXV) takes place preferentially *via* the iminolactone (XXVII):



In individual cases a single aminodeoxy-sugar is obtained; for example, threose gives chiefly 2-amino-2-deoxy-D--xylose[69]. The action of alkali on *N*-phenyl-D-hexosaminic [2-deoxy-2-phenylamino-D-hexonic (Ed. of Translation)] nitriles (XXVIII) gives iminohexose-2,3-ene-1→4-lactones (XXIX), which are hydrogenated to 2-amino-2,3-dideoxyhexoses (XXX)[70]:

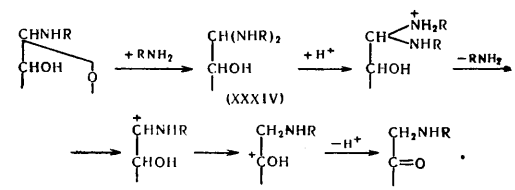


(b). The Amadori rearrangement and the reverse reaction. The Amadori rearrangement — the conversion of the *N*-glycosides of aldoses (XXXI) into *N*-substituted 1-amino-1-deoxyketoses (XXXII) — is the most effective method for preparing the compounds (XXXII)[13,16,71,72]:

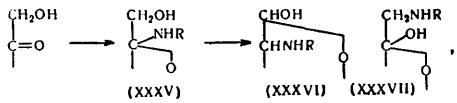


The yield of product increases with increase in the basic strength of the amine used for the formation of the *N*-glycoside[73,74]. The reaction was first applied to *N*-aryl glycosides, but was later extended to the *N*-alkyl derivatives[75-77], the derivatives of aliphatic-aromatic amines[78], and to amino-acids, from which 1-carboxyalkylamino-1--deoxyketoses (XXXIII) are formed[79-81]. Compounds of type (XXXIII) are of particular interest, since they have been found in liver and in micro-organisms[82]. The *N*-glycosides of uronic acids are converted into *N*-subtituted keto--acids in analogous fashion[83,84].

According to Micheel[85], the mechanism of the Amadori rearrangement includes a stage involving the intermediate formation of the *NN*-diacetal (XXXIV), which adds on a proton and undergoes further conversion according to the scheme:



The reaction which is the reverse of the Amadori rearrangement has been studied chiefly by Heyns and coworkers. This reaction, which is catalysed by acids or salts, makes it possible to obtain 2-amino-2-deoxyaldoses and their derivatives from ketoses. The reaction takes place with a ketosylamine or with *N*-alkyl ketosides (XXXV), including derivatives of amino-acids and peptides [86-89]:



(XXXV) (XXXVI) (XXXVII)

where R = H, alkyl, or CH(R')COOH.

Fructosylamine gives a mixture of glucosamine and mannosamine; the reaction of fructose with amino-acids gives the corresponding 2-carboxyalkylamino-derivatives of the epimers (XXXVI). The *N*-derivatives of 1-amino--1-deoxyketoses (XXXVII) are formed simultaneously.

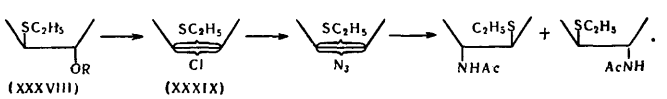
The theories of the Amadori rearrangement have been used to explain the mechanism of the complex reactions involved in the biosynthesis of aminodeoxy-sugars [16,90] and amino-acids [91] and also the reaction of melanoidin formation (the Maillard reaction) [16,92-94].

3. The Introduction of Nitrogen-Containing Groups into a Sugar and Conversion of the Former to Amino-Groups

(a). Conversion of sugar phenylhydrazones into aminodeoxy-sugar alcohols. New methods for bringing about this change have been developed [95]. Aminodeoxy-sugars are obtained by the reduction of the phenylhydrazones [95,96] or oximes [97] of the oxo-derivatives of monosaccharides. In connection with the development of a method for the selective oxidation of aldoses to 4-oxo-aldoses, the use of the latter for the synthesis of 4-amino--4-deoxyaldohexoses has been reported [98].

The usual method for the addition of nitromethane to aldoses makes it possible to obtain nitro-compounds which can be hydrogenated to amines. When applied to 5-formyl--1,2-*O*-isopropylidene-D-xylose, this method gave a mixture of stereoisomeric 6-amino-6-deoxy-D-glucose and -L-idose [99].

(b). Alcoholic hydroxyl groups in a sugar molecule can be replaced (*via* the sulphonyl group or a halogen atom) by azido-, cyano-, phthalimido-, and other groups, which are then converted into an amino-group in the usual way. For example, 6-amino-6-deoxy-D-glucose was obtained from the 6-*p*-toluenesulphonate of α-methyl glucoside *via* the azido-derivative [33]. Baker and coworkers [100] introduced the azido-group using the episulphonium ion (XXXIX) obtained by the action of thionyl chloride on the ethylthio-derivative of sugar sulphonates (XXXVIII):



(XXXVIII) (XXXIX)

Isomerisation and reversal of configuration take place during the reaction. An interesting feature is that similar changes take place in the molecules of nucleosides [101].

Recently, Baker and coworkers [102] showed that the methanesulphonyl group on a secondary carbon atom can be replaced directly by an azido-group and this made it possible to prepare derivatives of 4-amino-4-deoxy-D-glucose.

The phthalimide method has not been widely used, although the dimethylformamide used as solvent makes it possible to carry out the reaction between the sugar sulphonates and potassium phthalimide under comparatively mild conditions (at 90° and below); the phthalimido-derivatives of the aminodeoxy-sugars or aminodeoxy-sugar alcohols are split by heating with hydrazine in alcoholic solution [45].

The reaction of sugar sulphonates with ethyleneimine has given the ethyleneimino-derivatives, and from these the β-chloroethylamino-derivatives, which are of interest as anti-cancer agents (see below) [103].

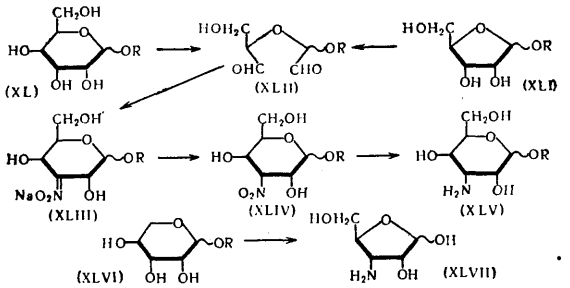
The condensation of monosaccharides with acrylonitrile (with subsequent hydrogenation of the condensation products) [39] or with esters of crotonic acid, with subsequent addition of an amine across the double bond [104] has been described.

Alkyl radicals containing amino-groups have been introduced into cellulose using epoxy- and diaminoepoxy-amines, which add on at the position of the hydroxyl groups [105,106].

A primary sulphonyl group can be replaced by a cyano--group either directly or *via* the iodide; the iodo-derivative can also be converted into the nitro-compound by substitution [107]. It is evidently possible to obtain amino-derivatives of sugars containing the $CH_2-CH_2-NH_2$ group, by hydrogenation of the resulting cyano-derivatives.

(c). The preparation of aminodeoxy-sugars from monosaccharides *via* uronic acids and their nitriles, which can be reduced to aminodeoxy--sugars, has also been carried out. This method has been used to synthesise 2,6-diamino-2,6-dideoxy-D-glucose (neosamine) from glucosamine derivatives [108]. Uronic acids are readily obtained by the catalytic oxidation of aldoses with oxygen according to Heyns' method [109].

(d). The synthesis of 3-amino-3-deoxymonosaccharides from dialdehydes, which are formed by the periodate oxidation of hexose and pentose glycosides and cyclised to the 3-nitro-derivatives of aldoses by the action of nitromethane, has also been developed. Hexopyranosides (XL) or pentafuranosides (XLI), *via* the dialdehydes (XLII), give the nitro-derivatives of the hexoses (XLIV), which give the corresponding 3-amino-3-deoxyhexoses (XLV) [110]. The pentapyranosides (XLVI) give dialdehydes which are converted into 3-amino-3-deoxy--pentoses (XLVII) [111]:



(XL) (XLII) (XLI)

(XLIII) (XLIV) (XLV)

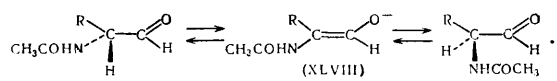
(XLVI) (XLVII)

A method has been found for the spontaneous epimerisation, at the C_4 atom, of the sodium derivatives of nitro--compounds (XLIII) by allowing the compounds to stand in

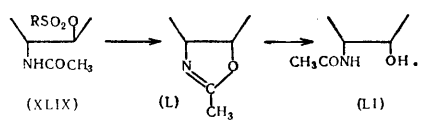
aqueous solution. From methyl α-D-glucopyranoside this method gave a mixture of the 3-amino-derivatives of D-glucose, D-mannose, D-galactose, and D-talose, in which the last two predominated[112]. Laevoglucosan gave a mixture of stereoisomeric 3-amino-1,6-anhydro-3--deoxy-hexoses with the gulo-, altro-, and ido-configurations[113]. Phenylhydrazine can be used instead of nitromethane for cyclisation of the dialdehyde, followed by hydrogenolysis of the resulting azo-compound[114].

4. Methods for Converting Aminodeoxy-Sugars into Other Aminodeoxy-Sugars and Aminodeoxy-Sugar Alcohols

(a). Epimerisation of aminodeoxy-sugars. It has been found possible to carry out the direct epimerisation of *N*-acetylglucosamine to *N*-acetylmannosamine[115] and of *N*-acetyl-D-galactosamine to *N*-acetyl-D-talosamine[116]. In the presence of 0.7 *N* ammonium hydroxide solution, 2-acetamido-2-deoxy-D-ribose is converted into an equilibrium mixture with the epimer in the ratio 2 : 1. The same equilibrium is established starting from the epimeric 2-acetamido-2-deoxy-D-arabinose. The corresponding monosaccharides are not epimerised under these conditions. The ease of conversion in the case of acetamidoaldoses is due to the inductive effect of the acetamido--group; it is assumed that an intermediate enolate ion (XLVIII) is formed[117]:



(b). Walden inversion in substitution reactions of aminodeoxy-sugars and aminodeoxy--sugar alcohols. Solvolysis of the α-sulphonates of *N*-acetylated aminodeoxy-sugar or aminodeoxy-sugar alcohols with these groups in the *trans*-position (XLIX) takes place with Walden inversion *via* the intermediate oxazoline ring (L), which is subsequently broken to give the *N*-acetyl aminodeoxy-sugars or aminodeoxy-sugar alcohols (LI) with the inverse configuration[118].



In practice, solvolysis is brought about by the action of sodium acetate with heating in a medium of methylcellosolve (2-methoxyethanol). This method is widely used in synthesis[119–123].

(c). Increase and decrease in the length of the aminodeoxy-sugar chain by the usual methods makes possible conversion from the 2-amino- to the 3-amino-derivatives of aldoses and back again. Thus Kuhn and coworkers, who increased the length of the carbon chain by the action of hydrogen cyanide, prepared 3-amino--3-deoxy-hexoses and -heptoses from the corresponding 2-amino-2-deoxy-pentoses and -hexoses respectively[124,125]. On the other hand, oxidation of the 3-amino-derivatives with periodate gave the 2-amino-2-deoxyaldoses; the latter are also formed by oxidising the corresponding thioacetals with peroxypropionic acid[126].

TABLE 1. Synthetic aminodeoxy-sugars and *N*-substituted aminodeoxy-sugars (obtained in the free form and as the *O*- and *N*-derivatives)*.

Sugar	Position and name of nitrogen-containing groups	References
1	2	3
I. Aminodeoxy-derivatives of sugars		
D-Threose	2-amino	131, 132
D-Erythrose	2-amino	131, 132
D-Arabinose	2-amino	69
D-Arabinose	3-amino	119
L-Arabinose	2-amino	133
L-Arabinose	3-amino	125
L-Arabinose	5-amino	134
D-Xylose	2-amino	69
D-Xylose	3-amino	131
D-Xylose	5-amino and substituted 5-amino	95, 96, 135, 136
D-Xylose	2,5-diamino	136
D-Lyxose	2-amino	38, 69
L-Lyxose	2-amino	42
D-Ribose	2-amino	38, 69, 117
D-Ribose	3-amino	111, 119, 137
D-Ribose	5-di-(2-chloroethyl)amino	103, 138
D-Ribose	5-(2-chloroethyl)ethylamino	138
D-Ribose	3,5-diamino	38
L-Ribose	2-amino	40
L-Ribose	3-amino	111
D-Allose	2-amino	19, 67
D-Allose	3-amino	27, 37, 53, 97, 113
D-Allose	3-ethylamino	139
D-Allose	3-ethyl-(2-chloroethyl)amino	139
D-Allose	3-(2-chloroethyl)amino	139
D-Allose	2,3-imino	57
D-Altrose	2-amino	19, 43, 140
D-Altrose	2-methylamino	43
D-Altrose	2-guanidino	43
D-Altrose	3-amino	56, 113, 126
D-Galactose	2-amino	19
D-Galactose	3-amino	112, 125
D-Galactose	6-amino	36, 141
D-Galactose	6-methylamino	39
D-Galactose	6-dimethylamino	142
D-Galactose	substituted 6-arylamino	36
D-Galactose	6-di-(2-chloroethylamino)	103
D-Glucose	2-amino and substituted 2-amino	19, 93
D-Glucose	3-amino	97, 112, 114
D-Glucose	3-dimethylamino	143
D-Glucose	4-amino	102
D-Glucose	6-amino	33, 50, 55, 99
D-Glucose	substituted 6-alkylamino	50, 144
D-Glucose	6-phenylamino	138
D-Glucose	6-benzylamino	138, 144
D-Glucose	6-dibenzylamino	51, 144
D-Glucose	5-pyridino	145, 146
D-Glucose	6-morpholino	51
D-Glucose	6-pyrrolidino	51
D-Glucose	6-piperidino	51, 144
D-Glucose	6-guanidino	50
D-Glucose	substituted 6-(2-chloroethyl)-amino	55, 138
D-Glucose	6-anilino	147
D-Glucose	2,6-diamino	108
L-Glucose	2-amino and substituted 2-amino	19
D-Gulose	2-amino	19, 60
D-Gulose	3-amino	113, 122, 125
L-Gulose	2-amino	19
D-Idose	2-amino	19, 52, 54
D-Idose	3-amino	52, 113, 122
L-Idose	2-amino	19
L-Idose	3-amino	122
L-Idose	5-amino	148
L-Idose	6-amino	99
D-Mannose	2-amino and substituted 2-amino	19, 59, 68, 93
D-Mannose	3-amino	112, 124, 149
D-Mannose	4-amino	8
D-Mannose	2,3-diamino	150
L-Mannose	2-amino	19, 59
D-Talose	2-amino	19, 54, 67
D-Talose	3-amino	112
D-Gluco-D--guloheptose	3-amino	125
D-Gluco-D--idoheptose	3-amino	125
D-Manno-D--galaheptose	3-amino	125
D-Threopentulose	5-amino	129
D-Erythropentulose	5-amino	129
L-Xylohexulose	5-amino	130
L-Xylohexulose	6-methylamino	130
L-Sorbose	1-amino and substituted 1-amino	71
D-Tagatose	1-amino and substituted 1-amino	76, 83, 89, 103, 151–153
D-Fructose	1-amino and substituted 1-amino	76, 83, 89, 103, 151–153
II. Aminodeoxy-derivatives of deoxy-sugars		
2-Deoxy-D-ribose	3-amino	100
6-Deoxy-D-altrose	3-amino	154
3-Deoxy-D-galactose	2-amino	70

TABLE 1. (cont'd).

Salt	Position and name of nitrogen-containing groups	References
1	2	3
II. Aminodeoxy-derivatives of deoxy-sugars		
6-Deoxy-L-galactose	2-amino	155, 156
6-Deoxy-L-galactose	3-amino	157
6-Deoxy-D-glucose	2-amino	158
6-Deoxy-D-glucose	3-amino	159
6-Deoxy-D-glucose	3-dimethylamino	159, 160
4,6-Dideoxy-D--glucose	3-dimethylamino	161
6-Deoxy-L-glucose	2-amino	158
6-Deoxy-L-glucose	3-amino	157
6-Deoxy-L-glucose	3-dimethylamino	159
3-Deoxy-D-mannose	2-amino	70
6-Deoxy-D-mannose	3-amino	162, 163
6-Deoxy-D-talose	2-amino	164
6-Deoxy-L-talose	3-amino	157
6-Deoxy-L-xylo-hexulose	5-amino	130
3-Deoxy-D-fructose	1-amino	165

* *Note added in proof*. Data have also been published on the synthesis of 2-amino-2-deoxy-L-xylose[286], 2,6-diamino-2,6-dideoxy-D-galactose[287], 2,4-diamino-2,4-dideoxy-D-glucose[288], 2,6-diamino-2,6-dideoxy-L-idose[289], 3-amino-3-deoxy-D-altro-γ-mannoheptose, 3-amino-3-deoxy-D-manno-D-taloheptose[290], 2,7-anhydro-4-amino-4-deoxyheptoses[291], 3-amino-3,5-dideoxy-L-idose[292], 2-amino-2,6-dideoxy-D-mannose[293], and 2-amino-2,6-dideoxy-D-talose[294]; improvements have been introduced in the synthesis of 6-amino-6-deoxy-D-glucose[295], 2-deoxy-2-amino-D-talose (talosamine)[116], 2-amino-2,6-dideoxy-L-mannose (L-rhamnosamine)[293], 2-amino-2,6-dideoxy-D-talose[294], 4-amino-4-deoxy-L-erythrose[303], 4-amino-4-deoxy-D-lyxose[304], 6-amino-6-deoxy- and 1,6-diamino-1,6-dideoxy-L-sorbose[305], 3-amino-3,5-dideoxy-D-xylose[306], derivatives of 5,6-diamino-5,6-dideoxy-D-glucose and -L-idose[307], 6-amino-6-deoxy-D-glucose[295], and 2-amino-2-deoxy-D-talose (talosamine)[116]. Data have also been published on the preparation of amino-derivatives of starch[308,309] and cellulose[310].

Decrease in the length of a chain with a non-reducing end is brought about by oxidising aminohexose furanosides with periodate, followed by reduction of the ω-formyl group. Finally, a combination of methods involving increase in the length of a chain, followed by decrease in the length of a chain with a non-reducing end, makes it possible to bring about "migration" of the amino-group — conversion of 2-amino-2-deoxyhexoses to 3-amino-3-deoxy-hexoses and -pentoses[125].

(d). Reduction of aminodeoxy-sugars and oxidation of aminodeoxy-sugar alcohols. The reduction of 1-amino-1-deoxyketoses gives an individual aminodeoxy-sugar alcohol or a mixture of aminodeoxy-sugar alcohols, depending on the conditions[127] (examples of the reduction of aminoaldoses are given by Foster *et al.*[128]). 1-Acetamido-1-deoxyketoses have been prepared by the oxidation of 1-acetamido-1-deoxy-sugar alcohols with *Acetobacter suboxydans* enzymes[129,130].

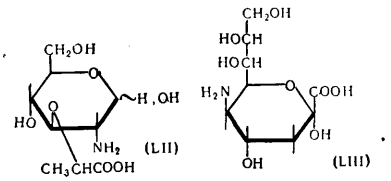
Thus there are at present a number of methods for preparing aminodeoxy-sugars with amino-groups on primary carbon atoms and on secondary carbon atoms in the 2- and 3-positions, and also the corresponding aminodeoxy-sugar alcohols. Methods for the synthesis of aminodeoxy-sugars with an amino-group on the fourth carbon atom (for pentoses and hexoses) and on the fifth carbon atom (for hexoses) have been little developed.

Table 1 gives the synthetic aminodeoxy-sugars and their *N*-substituted derivatives (with alkyl, aryl, or heterocyclic substituents) described in the literature¶. Many of these substances have been prepared in recent years[18]. The aminodeoxy-sugars can conveniently be divided into two groups: (1) aminodeoxy-derivatives of sugars, and (2) aminodeoxy-derivatives of deoxy-sugars, and can be further classified in the usual way as aldoses and ketoses, and as tetroses, pentoses, hexoses, and heptoses. Within the subgroups, the aminodeoxy-sugars are arranged in the alphabetical order of the monosaccharides [this refers to the Cyrillic alphabet; the order of the Russian version is retained in the translation and is no longer alphabetical (Ed. of Translation)].

III. AMINODEOXY-SUGARS OF NATURAL ORIGIN

Aminodeoxy-sugars are obtained from the degradation of a number of complex natural products present in animal and vegetable organisms, micro-organisms, soil substances, and antibiotics. In natural substances the primary amino-group of the aminodeoxy-sugars are usually acylated, most frequently with an acetic acid residue but also with sulphuric and other acids. A list of aminodeoxy-sugars of natural origin is given in Table 2.

Table 2 shows that, together with glucosamine and galactosamine, which are the most commonly-encountered nature aminodeoxy-sugars, the other aminodeoxy-sugars are also in most cases aminodeoxyaldohexoses. Only a few representatives of other types of aminodeoxy-sugars are encountered. Deoxygenated aminodeoxy-sugars with methylene and methyl groups are fairly widespread, and *N*-alkylated (methylated) aminodeoxy-sugars and diamino-derivatives are also encountered. In addition to aminodeoxy-sugars in the true sense, natural substances also contain the amino-acids: 2-amino-2-deoxy-D-galacturonic acid, muramic acid (LII), and sialic acids — the *N*-acyl derivatives of neuraminic acid (LIII). The latter are genetically related to mannosamine, which is formed when these acids are degraded.



In living organisms, aminodeoxy-sugars are found chiefly in the so-called mucoid substances. These include glucosamine, galactosamine, and sialic acids, together with other sugars, hexuronic acids, amino-acids, and lipids. Mucoid substances are usually subdivided into mucopolysaccharides, mucoproteins, and mucolipids, depending on the quantity of the corresponding components present[167]. There is, however, no generally-accepted classification. The term mucopolysaccharide (or amino-polysaccharide[208]) denotes a heteropolysaccharide with a high aminodeoxy-sugar content, and this class is subdivided into acidic (containing

¶ In general, only the latest published data for a given substance are quoted.

TABLE 2. Aminodeoxy-sugars of natural origin.

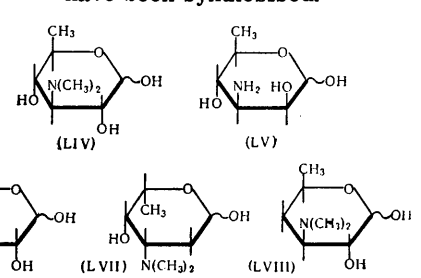
Name	Occurrence in natural products
3-Amino-3-deoxy-D-ribose	the antibiotic puromycin [166]
2-Amino-2-deoxy-D-galactose (galactosamine)	mucoid substances [14,167], bacteria polysaccharides [24], oligosaccharides of human milk [22], soil substances [168]
2-Amino-2,6-dideoxy-D-galactose (fucosamine)	bacteria polysaccharides [24,169]
2-Amino-2,6-dideoxy-L-galactose	bacteria polysaccharides [156]
2-Amino-2-deoxy-D-galacturonic acid	bacteria polysaccharides [24,170]
2-Amino-2-deoxy-D-glucose (glucosamine)	mucoid substances [14,167], bacteria polysaccharides and nucleotides [23,24], fungi, chitin of insects and crabs [21], oligosaccharides of human milk [22], soil substances [168], the antibiotics trehalosamine [171], paromomycin [172], racemomycin O [173], monomycin [174], and zygomycin [175] *
3-Amino-3-deoxy-D-glucose (kanosamine)	the antibiotics kanamycin A [176,177] kanamycin B [178], and kanamycin C [179]
6-Amino-6-deoxy-D-glucose	the antibiotic Kanamycin A [176]
3-Dimethylamino-3,6-dideoxy--D-glucose (mycaminose)	the antibiotics magnamycin (carbomycin), leucomycin [180], spiramycin [181]
2,6-Diamino-2,6-dideoxy-D--glucose (neosamine C)	the antibiotics neomycin C [182,183], zygomycin [184]*, paromomycin II [194]
2-Amino-2-deoxy-3-*O*-(2--carbethoxy)-D-glucose (muramic acid)	bacteria nucleotides and polysaccharides [23,24]
3-Dimethylamino-3,4,6--trideoxy-D-xylohexose (desosamine, picrocine)	the antibiotics methymycin [185], neomethymycin [186], picromycin [187], erythromycin A [188], erythromycin B [189], erythromycin C [190], oleandomycin [191], narbomycin [192]
2-Methylamino-2-deoxy-L--glucose	the antibiotics streptomycin, dihydrostreptomycin, hydroxystreptomycin, mannosidostreptomycin [11,64]
2-Amino-2-deoxy-D-gulose (gulosamine)	the antibiotic streptomycin [193]
2,6-Diamino-2,6-dideoxy-L--idose (paromose)	the antibiotics neomycin B, paromomycin I [194,311]
2-Amino-2-deoxy-D-mannose (mannosamine)	product of the enzymatic breakdown of sialic acids [195]
3-Amino-3,6-dideoxy-D--mannose (mycosamine)	the antibiotics nystatin [196], amphotericin B [197], pimaricin [198], trichomycin [199], candinin, candicidin [200]
Sialic acids	mucoid substances [14,195], bacteria polysaccharides [24], oligosaccharides of human milk [22]
2-Amino-2-deoxy-D-talose	mucoid substances [201]
2-Amino-2,6-dideoxy-D--talose (pneumosamine)	bacteria polysaccharides [164]
1-Deoxy-1-*N*-*o*-carboxyphenyl-ribulose	bacteria polysaccharides [202]
Substituted 1-amino-1-deoxy--D-fructose	liver [82]
4-Dimethylamino-4,6-dideoxy--D-glucose (amosamine)	the antibiotic amicetin [203]
3-Dimethylamino-2,3,6--trideoxy-L-lyxohexose (rhodosamine)	antibiotics rhodomycin, isorhodomycin [204,205], pyrromycin [206]
2-Amino-4-acetamido-2,4,6--trideoxyhexose	bacteria polysaccharides [207]

aminodeoxy-sugars themselves, hexuronic acids, and sulphuric acid) and "neutral" (containing aminodeoxy-sugars and sialic acids) compounds. Mucoproteins (mucoids) are complex proteins with mucopolysaccharides as prosthetic groups. The name glycoproteins has also been suggested for these substances [208]. Mucoid substances are sometimes subdivided into: (1) glycoproteins, (2) mucoproteins, and (3) mucoproteids [209]; the first two types of substance have strong covalent bonds between the carbohydrate and protein components, whereas the mucoproteids are complexes formed by polysaccharides and proteins by ionic and hydrogen bonds. Mucoid substances are present in the materials characterising the blood group (group-specific polysaccharides), in blood serum, in the material of the salivary gland, urine, connective tissue, the secretions of the sexual organs, the epithelial mucus of the digestive tract, and are components of enzymes, hormones, malignant growths, etc. [167].

The aminodeoxy-sugars found in bacteria include, in addition to glucosamine, galactosamine, muramic acid, and sialic acids, other less common aminodeoxy-sugars: 2-amino-2,6-dideoxy-D-galactose and -L-galactose, 2-amino-2,6-dideoxy-L-talose, etc. Here the aminodeoxy--sugars are components of polysaccharides and nucleotides [23,24].

An even greater variety of aminodeoxy-sugars is found in antibiotics, chiefly macrolides, streptomycins, and streptomycin-like antibiotics [64]. Antibiotics containing aminodeoxy-sugars generally have the chemical structure of *O*-glycosides of aminodeoxy-sugars; the antibiotic puromycin is an *N*-glycoside (nucleoside) of 3-amino-3-deoxy--D-ribose.

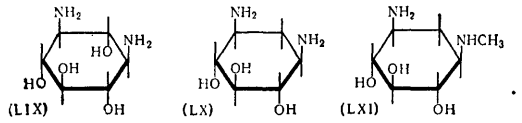
Work carried out in recent years has reduced considerably the list of aminodeoxy-sugars of unknown configuration and has revealed the nature of many aminodeoxy-sugars present in antibiotics. Thus it has been shown that the *N*-dimethylaminodeoxyhexose mycaminose, found in magnamycin (carbomycin) and other antibiotics and previously assigned the configuration of a D-altrose, is in fact 3,6-dideoxy-3-*N*-dimethylamino-D-glucose (LIV) [159,160]. Mycosamine (the aminodeoxyhexose of the antibiotics nystatin, pimaricin, etc.) is 3-amino-3,6-dideoxy-D-mannose (LV) [162,163]. The structure of two other aminodeoxy--sugars present in antibiotics — amosamine and rhodosamine — has recently been established. The former, a 4-aminohexose, is 4,6-dideoxy-4-dimethylamino-D-glucose (LVI) [203] and the latter is 2,3,6-trideoxy-3-dimethylamino-L--lyxohexose (LVII) [204]. It has been established by degradation, study of the nuclear magnetic resonance spectra, and synthesis that the extremely widespread amino-sugar desosamine (picrocine) is 3,4,6-trideoxy-3-dimethylamino-D-xylohexose (LVIII) [210-213]. Muramic acid [214,215] and *N*-acetylneuraminic acid [116,216] have been synthesised.



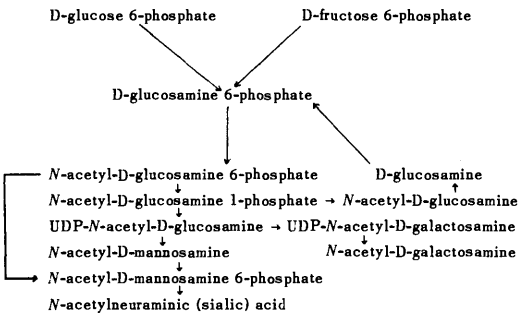
Among the substances related to aminodeoxy-sugars and found in natural products, not including riboflavine [62], are

* *Note added in proof.* Zygomycin was found to be idential with paromomycin [194,312].

the cyclic aminodeoxy-alcohols: streptamine (LIX) (in streptomycin and related antibiotics), 2-deoxystreptamine (LX) (in kanamycins, neomycins, and paromomycin), neo-inosamine-2 (IV) (in hygromycin)[5], 2-deoxy-*N*-methylstreptamine (LXI) (in hygromycin B [217]) and tetrahydroxy-1,3-bismethylaminocyclohexane (in the antibiotic actinospectacin)[218]:



The biosynthesis of aminodeoxy-sugars has been described in a number of reviews[17,208,219,220]. Glucosamine 6-phosphate is formed from the 6-phosphates of D-glucose or D-fructose using L-glutamine or ammonia[221]. Galactosamine is formed from glucosamine, as the uridine diphosphate (UDP) of the *N*-acetyl derivative; there are no data confirming that galactosamine is formed from galactose. On the other hand, there are enzymes which catalyse the conversion of glucosamine derivatives into mannosamine derivatives and the latter to sialic acids. These changes are outlined in the following simplified scheme:



Vitamin A plays an important part in the biosynthesis of aminodeoxy-sugars; it has also been established that vitamin C deficiency leads to an increase in the concentration of sialic acids and hexosamines in the organism[208]. The UDP-*N*-acetylglucosamine takes part in the formation of chitin[222].

IV. CHEMICAL REACTIONS AND PREPARATION OF DERIVATIVES OF AMINODEOXY-SUGARS

The most detailed studies have been made of the chemical reactions of 2-amino-2-deoxyaldoses, particularly glucosamine (reviewed by Foster and Horton[18]), and the genetically related 1-amino-1-deoxyketoses. Much attention is paid to the synthesis of the *N*-acyl derivatives of glucosamine, particularly with nature amino-acid residues, since these are models of glycopeptides[223-225]. A method has been developed for the selective *N*-acylation of aminodeoxy-sugars with carboxylic acids and amino-acids without blocking of the hydroxyl groups of the aminodeoxy-sugars[223,224]. *N*-Sulphonated aminodeoxy-sugars are being studied in detail[236,237].

The 2,5-dinitrophenyl[238], benzylsulphonyl[239], *N*-formyl[240], and ethoxycarbonyl[241] groups have been proposed for the protection of the amino-group in aminodeoxy-sugars. The *N*-methylation of *N*-acetylglucosamine has been described[242].

Analogues of glucosamine, containing urea and thiourea residues in place of the amino-group, have been synthesised; the urea-derivatives have been cyclised to the corresponding tetrahydroimidazole derivatives[243], which are also obtained by the action of isocyanates on glucosamine and 1-amino-1-deoxyfructose[244,245]. The preparation and hydrogenation of the Schiff's bases of glucosamine have been studied[246]. A number of new *N*-glucosaminides have been prepared[247], particularly *O*-β-(D,L-*trans*)-2-aminocyclohexyl glucosaminide[248], as a model of the antibiotic kanamycin.

The rate of hydrolysis of methyl glucosaminides has been studied[249]; it was found that the rates of hydrolysis and oxidation of methyl *N*-acylglucosaminides are lower, the stronger the acid forming the acyl residue; steric factors influence the oxidation[250]. 1-Chloro-substituted *N*-acylglucosamines with different acyl groups[251,252] and 1-*C*-phenyl-substituted glucosamine[253], 1-thioglucosamine[254], thioglucosaminides[255], and glucosamine 1-phosphate[256] have been prepared. It has been shown that the *O*-acetyl derivatives of glucosamine with a free amino-group are unstable: solvolysis at the $C_{(3)}$ atom takes place in alcholic solution under ordinary conditions[257]. 6-Thioglucosamine has been synthesised[258].

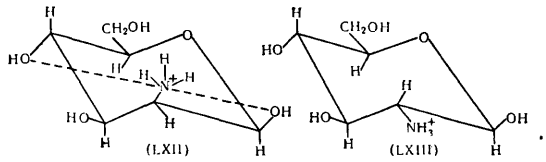
The conversion of aminodeoxy-sugars into imidazole derivatives and other heterocyclic compounds has been reviewed[259]. The action of aqueous ammonia converts glucosamine into a mixture of pyrazines[260]; pyrazines are also formed when the acetates of glucosamine or 1-amino-1-deoxyfructose are boiled in methanol[165]. As in the case of sugars without nitrogen-containing groups, lime water converts oligosaccharides containing glucosamine residues attached by 1,4-bonds into a mixture of different isosaccharinic acids[261].

Deamination of methyl 4,6-*O*-benzylideneglucosaminide with nitrous acid gives 2,5-anhydro-4,6-*O*-benzylidene-D-mannose, *i.e.* deamination is accompanied by splitting of the glycoside bond, whereas the corresponding altroside is converted into methyl 2,3-anhydro-4,6-*O*-benzylidene-D-alloside[241].

Synthetic polymers of glucosamine have also been prepared[262].

The Amadori rearrangement is still being actively studied[263]. Combination of Amadori products containing aromatic radicals with diazonium salts give triazines[264,265] or azo-compounds as a result of reaction with the aromatic nucleus[265].

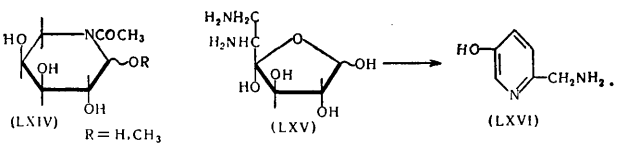
The basic strength of mannosamine is only one-third that of glucosamine, so that acylation of the former gives chiefly the *O*-acyl derivatives; mannosammonium chloride does not undergo mutarotation. This is due to the formation of a stable hydrogen bond between the ammonium- and the 1- and 4-hydroxyl groups in mannosamine (LXII); this bond is not present in glucosamine (LVIII)[266]:



The characteristic features and properties of aminodeoxy-sugars with structures different from those of 2-amino-2-

deoxyaldoses and 1-amino-1-deoxyketoses have been little studied. As in the case of glucosamine, the screening action of the $-NH_3^+$ group in a number of cases hinders the acid hydrolysis of the *O*-glucosides and acetals (ketals) of aminodeoxy-sugars, so that usually the *N*-acylated derivatives are subjected to hydrolysis. Depending on the structure of the molecule, however, reaction is also possible with substances containing a free amino-group: methyl 3-amino-3-deoxy-α-D-talopyranoside is converted into the aminodeoxy-sugar hydrochloride by heating with 2 *N* HCl at 98° for 2 h,[112] *i. e.* the reaction is similar to that with ordinary glycosides. Methyl 3-amino-3,6-dideoxy-D-altroside (2 *N* HCl, 12 h, 100°)[154] and methyl 3-amino-3-deoxy--D-glucoside (4 *N* HCl, 100°, 3 h)[177] are hydrolysed similarly. The hydrolysis of the analogous glycosides of 3-amino-3-deoxy-D-xylose and -D-ribose requires heating for a prolonged period (18–22 h) in 1 *N* HCl.[135] The reaction takes place comparatively readily when combined with anhydride-formation; the tendency to form 1,6-anhydrides is more marked for 3-amino-3-deoxyaldoses than for the corresponding 2-amino-derivatives[122]†.

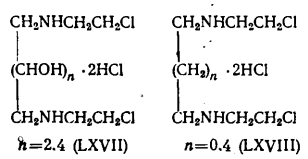
Very interesting results have recently been published on the cyclisation of aminodeoxy-sugars with an amino-group on the fifth carbon atom: 5-acetamido-5-deoxy-L-arabinose gives the cyclic form (LXIV) with an *N*-heteroatom[134]. Analogous results were obtained with 5-acetamido-5-deoxy--D-xylose[267,268]. In the case of 5-amino-5-deoxy-L-idose, however, only the *O*-furanoside bridge is formed[148]. 5,6--Diamino-5,6-dideoxyaldohexoses (LXV), at the moment of their formation, are converted into 2-aminomethyl-5--hydroxypyridine (LXVI)[61]:



(LXIV) (LXV) (LXVI)

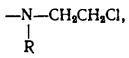
V. PRACTICAL APPLICATION OF AMINODEOXY-SUGARS AND AMINODEOXY-SUGAR ALCOHOLS

A number of aminodeoxy-sugar and aminodeoxy-sugar alcohol derivatives have been synthesised for use as drugs. To obtain anti-cancer agents, the *N*-β-chloroethyl group is introduced into the sugar molecules. The first and most active of these substances was 1,6-di-(2-chloroethylammonium)--1,6-dideoxy-D-mannitol dichloride, which was introduced into clinical practice under the name "Degranol"[269]. The synthesis of this compound and analogous compounds — derivatives of hexahydric and tetrahydric alcohols (LXVII)[270,271] — is achieved by replacing a sulphonyl group in the sugar or sugar alcohol molecule by an $NHCH_2CH_2OH$ or $N(CH_2CH_2OH)_2$ group followed by replacement of the hydroxyl by chlorine. In another method the ethyleneimine group is introduced and then split with hydrogen chloride. A more active compound than "Degranol" is its bromo-analogue — 1,6-di--(2-bromoethylammonium)-1,6-dideoxy-D-mannitol dibromide. Contrary to expectation, the corresponding iodo--derivative was found to have a low activity. Stereoisomers of "Degranol" — derivatives of D-sorbitol, dulcitol, D-iditol, and D-mannitol — are much less active; the dulcitol derivative shows the greatest activity.



It has been confirmed that a decisive part in the anti-carcinogenic activity of substances of this type is played by the system of hydroxyl groups of the polyhydric alcohol, since the corresponding β-chloroethylamino-derivatives of hexane and ethane (LXVIII) are quite inactive[269]. The further introduction of methanesulphonyl groups in the "Degranol" decreases the cumulative effect[272]. Vargha and coworkers also prepared di-*N*-(β-chloroethyl) derivatives of D- and L-glucosamine, 6-amino-6-deoxy-D-galactose, ethyl 5-amino-5-deoxy-D-ribofuranoside, 1-amino--1-deoxy-D-fructose and -L-sorbose; all these substances were found to be toxic[103]‡.

Baker and coworkers synthesised a number of derivatives of 6-amino-6-deoxy-D-glucose[55,138], 5-amino-5--deoxy-D-ribose,[138] and 3-amino-3-deoxy-D-allose[139] containing the group



where R = CH_2CH_2Cl (*a*), C_2H_5 (*b*) (for all the above aminodeoxy-sugars), H, CH_3 (*c*), etc. for 6-amino-6-deoxy-D--glucose. Of these compounds, activity against leukaemia 1210 was shown by the derivatives (*b*) for all aminodeoxy--sugars, (*a*) for the ribose and allose, and also by (*c*); in addition, the ribose derivative (*b*) was found to be active against adenocarcinoma 755. Analogous galactose derivatives of the urethane type, containing the $-OCON(CH_2CH_2Cl)_2$ group, have been prepared[273]. American workers have developed a programme for the synthesis of anti-cancer agents based on aminodeoxy-sugars[55].

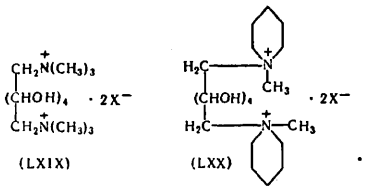
Nucleosides with aminodeoxy-sugars as components of their molecules have been synthesised: the antibiotic puromycin, which exhibits anti-cancer activity, and the possible antimetabolites 3′-amino-2′,3′-dideoxyadenosine and 2′-amino-2′-deoxyadenosine[101].

A number of derivatives of 1,6-dideoxy-1,6-bis(trimethylammonium)-D-sorbitol and -D-mannitol (LXIX) and 1,6-dideoxy-1,6-bis(methylpiperidino)-D-sorbitol (LXX) with *O*-isopropylidene and *O*-acyl substituents have been synthesised as potential drugs[274]. Some of these substances reduce the blood pressure slightly and also exhibit

† *Note added in proof*. Acetobromo-derivatives of 3-amino--3-deoxy- and 6-amino-6-deoxy-D-glucose have been synthesised[296]. The preparation of thioglycosides by the thiolation of 3-amino--3-deoxy-D-mannose has been described[297]. Glucosamine-3--phosphate has been prepared[298]. The kinetics of the alkaline decomposition of D-mannosamine have been studied[299]. Derivatives of 1,6-dithio-D-glucosamine have been synthesised[300]. The infrared spectra of some derivatives of 6-amino-6-deoxy-D-galactose and 5-amino-5-deoxy-D-xylose have been studied[301].

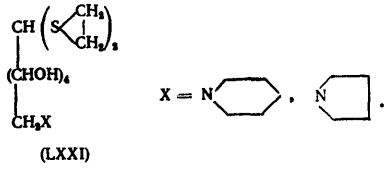
‡ *Note added in proof*. The 1,6-bis-di-*N*-(β-chloroethyl) derivative of L-sorbose was also found to be unsuitable for therapeutic purposes[302].

a weak antispasmodic, cholinergic, and curare-like action; the sorbital derivatives are more active than the mannitol derivatives.



(LXIX) (LXX)

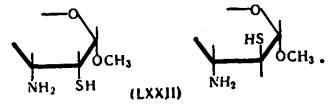
Hydrazides of *N*-acylglucosaminylisonicotinic acid, which are anti-tuberculosis agents, have been prepared[275]. A number of derivatives of the ethylene thioacetal of 6-amino-6-deoxyglucose (LXXI) have been synthesised in the search for anti-fungal materials. The 6-piperidino- and 6-pyrrolidino-derivatives were found to be active against the very resistant forms *Cryptococcus neoformanes* and *Aspergillus niger*:



(LXXI)

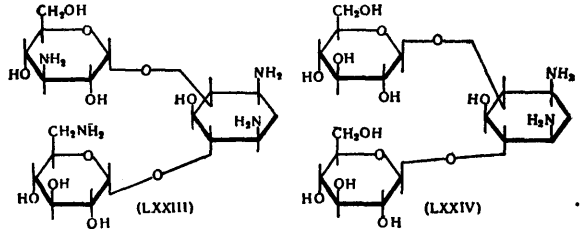
The importance of the nitrogen-containing residue is confirmed by the fact that the corresponding thioacetal of D-glucose is inactive[51].

2-Thiol derivatives of 3-amino-3-deoxy-D-allose[53] and -D-altrose (LXXII)[56] have been synthesised in the search for anti-radiation agents:



(LXXII)

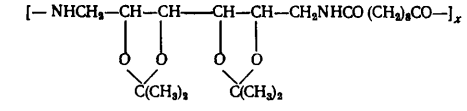
To investigate the influence of aminodeoxy-sugars on the activity of antibiotics, Umesawa and Ito[276] synthesised the anomer of kanamycin (LXXIII) without amino-groups in the glucose residue, 4,6-di(β-D-glucopyranosyl)-deoxystreptamine (LXXIV), which was found to be biologically inactive:



(LXXIII) (LXXIV)

The 1-alkylamino-derivatives of hexahydric alcohols[277], which are used as surface-active agents, are aminodeoxy--sugar alcohols which have been known for a long time. The corresponding aminodeoxy-sugar derivatives may be of interest as cationic surface-active agents.

The preparation of macromolecular compounds of the polyamide type from α,ω-diamino-sugar alcohols and derivatives of dibasic acids has been described. 1,6-Diamino--1,6-dideoxy-2,3:4,5-di-*O*-isopropylidenedulcitol with sebacoyl chloride gives a polymer (LXXV) which is insoluble in water and soluble in alcohol; after removal of the isopropylidene groups it is converted into an insoluble infusible product[278]:



(LXXV)

A large number of polyamides have been prepared by condensing 1,6-diamino-1,6-dideoxy-2,3:4,5-dimethylene-dulcitol, -D-mannitol, -D-sorbitol, -L-iditol and the analogous benzylidene derivatives with various dihydrochlorides, including the dihydrochlorides of dimethylenesaccharic acids[279,280].

Another type of polymer has been prepared from aminodeoxy-sugar alcohols acylated with unsaturated acids. 1-Acrylamido-1-deoxy- and 1-methacrylamido-1-deoxy--D-sorbitol have been polymerised with varius polymerisation initiators and also under the influence of ^{60}Co radiation. Water-soluble polymers and polymers assumed to have a "cross-linked" structure have been prepared. The above amides have been copolymerised with other vinyl derivatives[281]. Monomers of possible interest include the *N*-methacryl derivatives of 1-amino-1-deoxyxylitol and 2-amino-2-deoxyxylitan[30].

The present intensive study of aminodeoxy-sugars must lead to the production of valuable biologically active substances, polymers, surface-active agents, etc.

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THE CATALYTIC SYNTHESIS OF CARBOXYLIC ACIDS AND THEIR ESTERS FROM CARBON MONOXIDE, ALKENES, AND ALCOHOLS

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1. INTRODUCTION

More than 100 years have passed since Berthelot's discovery[1] of the reaction between carbon monoxide and caustic alkali to give formates:

$$CO+KOH \rightarrow HCOOK.$$

This process formed the basis of the modern industrial preparation of formic acid. Subsequently, during the first quarter of the 20th century, a number of new reactions of carbon monoxide were discovered, and these have played an important part in the development of organic synthesis. In these reactions, carbon monoxide and hydrogen in the presence of heterogeneous catalysts give either hydrocarbons — methane[2] or a mixture of higher aliphatic hydrocarbons of the synthine type[3] — or oxygen-containing compounds — methanol and its homologues[4] or mixtures of

aliphatic alcohols; aldehydes, ketones, and acids, of the synthol type[5,6]. Most of these processes have been applied in industry and are widely described in the literature.

In the past 20 years, new reactions of carbon monoxide have acquired considerable importance. The distinguishing feature of these reactions is that the carbon monoxide combines with another organic reagent, entering the molecule of the organic compound in the form of a carbonyl group. This leads to the production of a new oxygen-containing functional group — aldehyde, ketone, acid, ester, etc.

Reactions of this type include the formylation[7-9] of olefinic compounds with carbon monoxide and hydrogen to give aldehydes and alcohols. This reaction was discovered by Roelen[10,11] and is also known as the oxo-process:

$$R{-}CH{=}CH_2+CO+H_2 \longrightarrow \begin{matrix} R{-}CH_2CH_2CHO \\ R{-}CH(CHO)CH_3 \end{matrix}.$$

Even before this reaction was reported, chemists in the USSR carried out the hydrocondensation of carbon monoxide with alkenes[12-14]: in these reactions, carbon monoxide, hydrogen, and alkenes react to form olefinic and paraffinic hydrocarbons with higher molecular weight. Unlike the oxo-process, which is carried out at 150–200 atm in the presence of cobalt carbonyl, this process is carried out over a cobalt catalyst at atmospheric pressure.

In the oxo-process, hydrogen can be replaced by reagents containing labile hydrogen in the molecule.

The present review examines reactions which are being studied fairly widely abroad but only on a comparatively small scale in the USSR. These include the reactions of carbon monoxide with alcohols or ethylenic compounds and a third compound with a labile carbon atom, leading to the synthesis of carboxylic acids and their esters.

All these processes are catalytic and in most cases take place at high pressures. Important catalysts include acidic reagents such as phosphoric acid, sulphuric acid, and boron trifluoride, or nickel, cobalt, and iron compounds which during the reaction are converted into carbonyls or carbonyl hydrides, which are the true catalysts in these processes.

Some of these reactions were described in 1947[15] and in an article by Orchin and Wender in 1957.[16] Since then, however, new material has accumulated and a further review is necessary. A recent review by Bird[17] dealt only with reactions involving metal carbonyls, but almost no reference was made to the work reviewed in the present article.

2. REACTIONS OF CARBON MONOXIDE WITH ALCOHOLS

The direction of the reaction of carbon monoxide with alcohols depends to a considerable extent on the nature of the catalysts used and the conditions of the process. The reaction products may be formates:

$$CO+ROH \rightarrow HCOOR, \quad (1)$$

higher carboxylic acids:

$$CO+ROH \rightarrow RCOOH, \quad (2)$$

or their esters:

$$CO+2ROH \rightarrow RCOOR+H_2O.$$

According to Stähler[18], reaction (1) occurs with aliphatic alcohols at 40–190° and 120–400 atm, using the corresponding sodium alkoxide as catalyst. Later, potassium alkoxide was used for the same purpose[19,20]. The true catalyst in the reaction may, however, be the alkali metal formate[21], formed by Berthelot's reaction from carbon monoxide and the alkali metal hydroxide, into which the alkoxide is converted by moisture which is unavoidably present. The formate then reacts with the alcohol to form the formic ester and the alkali hydroxide:

$$HCOONa+ROH \rightarrow HCOOR+NaOH.$$

Reaction (1) possibly takes place under the influence of sodium hydroxide. It was reported[22] that methyl formate is formed from carbon monoxide and methanol at 100 atm in the presence of NaOH. This synthesis was studied[23] at 50–60°, 70–220 atm, and a $CO:CH_3OH$ molar ratio of 0.75–1.7. The apparent activation energy is 15.7 kcal mole^{-1}. Reaction (1), which also takes place with cyclic alcohols such as cyclohexanol and benzyl alcohol[24], is reversible[25]. The kinetics of the reaction have been studied in detail for methanol, ethanol, both propanols, and all four butanols[26,27]. The rate constants for the formation of formates from these alcohols at 40° are given in Table 1.

The alkoxides were prepared by dissolving metallic sodium in the corresponding alcohols. Metallic potassium was used only in the experiments with t-butanol, since sodium butoxide is sparingly soluble in this alcohol. Table 1 shows that the reaction rate is lowest for methanol and highest for s- and t-butanols. The reaction rates for primary alcohols with the iso-structure are double those for the corresponding normal alcohols.

At first a number of basic catalysts were used[28-30]. The reaction was carried out in the vapour phase at 250–500° and 50–300 atm in the presence of catalysts containing the oxides of various metals, chiefly from Groups IV and VI, together with alloys, particularly those of copper, silver, gold, and lead, or individual metals of Group VIII (iron, cobalt, or nickel), and also alkali or alkaline earth metal hydroxides. It was reported[31] that a 1% solution of sodium methoxide in methanol has been used as a catalyst to synthesise acetic acid in 80% yield from CO and methanol at 60–100° and 10 atm. It is doubtful if these data are correct, however. A large number of acidic catalysts were then proposed: inorganic acids (boric, arsenic, molybdic, uranic, phosphoric, tungstic, and titanic), hetero-acids (molybdophosphoric, tungstosilicic, molybdosilicic, uranosilicic, etc.), and the acid salts of these acids[15]. These catalysts are generally used on carriers (carbon, graphite, coke, or silica gel) and promoted with various metals, chiefly those of Group VIII but also copper, manganese, chromium, vanadium, and some Group IV metals (titanium, zirconium, and thorium). Metal salts have also been proposed as promoters, particularly the phosphates and

TABLE 1.

Original alcohol	Rate constant for the formate formation, $10^8 K$, s^{-1}
Methanol	81
Ethanol	288
Propanol	443
Butanol	411.5
Isopropanol	836.3
Isobutanol	884.8
s-Butanol	1473
t-Butanol	1098

arsenates of the Group II metals, copper, aluminium, manganese, and chromium. The oxides of various metals, containing metal nitrates or the methyl esters of the simplest carboxylic acids; halides, including fluorides, and other fluorine compounds, particularly boron trifluoride, have also been used. For example, dibasic carboxylic acids or their esters have been prepared[32] from aliphatic hydroxycarboxylic acids or their esters and CO in the presence of boron trifluoride at 75–300° and 400–1000 atm. The ratio of the original acid to boron trifluoride was 3 : 1 and the hydroxyl group should be separated from the carboxyl group by at least two carbon atoms. Adipic acid is formed from CO and butane-1,4-diol in the presence of BF_3 and H_3PO_4 at 300° and 300 atm.[33]

Dolgov and Abarenkova[34] concluded that basic catalysts bring about reaction (1) and acidic catalysts bring about reaction (2). The possibility that the reaction can take place in two directions depending on the nature of the catalysts was attributed to the ability of the alcohol to dissociate in two days with the formation of either a hydrogen cation or a hydroxide anion. In the first case, in the presence of basic catalysts, the reaction with carbon monoxide gives formates, and in the second case, under the influence of acidic catalysts, the reaction gives esters of higher acids. Thus, according to Dolgov and Abarenkova, acidic catalysts act as dehydrating agents. In the case of methanol, the alcohol can decompose to the methylene radical and water with the subsequent formation of the keten and then acetic acid:

$$CH_3OH \rightarrow \dot{C}H_2 + H_2O,$$

$$\dot{C}H_2 + CO \rightarrow CH_2{=}CO,$$

$$CH_2{=}CO + H_2O \rightarrow CH_3COOH.$$

These authors[34] prepared acetic acid from carbon monoxide and methanol in the presence of chromium metaphosphate deposited on a porous carrier. Under the optimum conditions (400° and 100 atm) the reaction product contained 13% of acetic acid.

Hardy[35] found that the formation of acetic acid from methanol vapour and carbon monoxide is exothermic. The heat of reaction is 24.84 kcal per mole of acetic acid in the vapour state. Earlier, on the basis of the calculated equilibrium constant, Shilov[36] concluded that the reaction is thermodynamically possible, and Hardy confirmed this conclusion by showing that the equilibrium favours the synthesis of acetic acid up to 370° at atmospheric pressure. Increase in pressure to 50 atm at 327° decreases the degree of decomposition of this acid from 25% to 4%. At 330–340° and 150 atm with circulation of the carbon monoxide in the presence of 87% phosphoric acid containing 2% copper phosphate, the reaction product contained 5.8% of acetic acid, 13.5% of methyl acetate, and 1.3% of dimethyl ether. The total yield of acetic acid and methyl acetate increased with increase in the quantity of catalyst, rate of circulation, and pressure. In experiments lasting 14 h, it reached 45% of the original quantity of methanol and 81% of the methanol reacting. The degree of conversion of the carbon monoxide in one passage was 0.5%. Up to 4.8% of the original methanol was converted into carbon during the reaction.

A large quantity of carbonaceous deposit was also observed by Singh and Krase[37] during the formation of acetic acid from CO and methanol in the vapour phase in the presence of phosphoric acid under pressure at 410–480°. They obtained the best results with active carbon impregnated with syrupy phosphoric acid. The rate of formation of acid in experiments with recirculation of the gas was double that in experiments with a flow system.

Lel'chuk and Karpov[38] studied a number of catalysts consisting of phosphoric acid on active carbon with various additives, for the synthesis of acetic acid from carbon monoxide and methanol at 350° and 200 atm in a circulation system. The additives were uranium and titanium nitrates and chromium phosphates and pyrophosphate. Molybdophosphoric acid was also used. The most active and stable catalyst was phosphoric acid containing uranium nitrate: the rate of formation of acetic acid amounted to 18.2 g h^{-1} and its concentration in the condensate was 12–18%. A number of undesirable products were formed simultaneously, including macromolecular aromatic compounds which caused sintering of the catalyst. The authors concluded that more stable or more readily regenerated catalysts should be used for this synthesis since the phosphoric acid catalysts have a low stability.

Acetic acid can be synthesised by the reaction of CO with $CH_3OH.BF_3$ at 160–220° and 765–1120 atm.[39] It was suggested that under these conditions $CH_3OH.BF_3$ is converted into $(CH_3)_2O.BF_3$ and $H_2O.BF_3$, which react with CO. The rate of formation of acetic acid is proportional to the $CH_3OH.BF_3$ concentration. The apparent activation energy is 15 kcal $mole^{-1}$. Under the optimum conditions (200°, 1000 atm, molar ratio $H_2O.BF_3 : CH_3OH.BF_3 = 1.5$, duration 2 h), the yield of acetic acid was 92%.

Hardy[40] used 87% phosphoric acid containing copper phosphate for the reaction of the homologues of methanol with carbon monoxide in a circulation system at 200 atm. From ethanol at 250–370° he obtained oily polymers of ethylene, some propionic acid and ethyl propionate, and traces of acetaldehyde and volatile hydrocarbons. n-Propanol and isopropanol at 200–250° were converted into a mixture of isobutyric acid, unsaturated hydrocarbons, isobutyl methyl ketone, and diisopropyl ketone. The yield of acids amounted to 40% or 46%, relative to the original alcohols (calculated on the carbon). Hardy concluded that these alcohols, before reacting with carbon monoxide, are dehydrated to propene, which simultaneously undergoes polymerisation to higher hydrocarbons and reacts with carbon monoxide and water vapour to form isobutyric acid (see p. 443). From the isomeric butanols, at 200–210° in the presence of the same catalyst, Hardy[41] obtained a mixture of trimethylacetic and ethylmethylacetic acids, higher ketones, and hydrocarbon polymers. The yield of acids relative to the weight of original alcohol amounted to 24%, 28%, and 22% in the experiments with n-butanol, s-butanol, and isobutanol respectively. In this case also it was assumed that the alcohols are first dehydrated with the formation of butenes, which simultaneously polymerise and react with CO and H_2O to form C_5 acids; mutual isomerisation of the butenes also takes place and this explains, for example, the fact that trimethylacetic acid is obtained from n-butanol.

Considerable progress in this field of chemistry was achieved when the carbonyls of Group VIII metals were first used as catalysts.

In 1941, Reppe and coworkers[42] showed that mixtures of a metal carbonyl and halide act as effective catalysts in the synthesis of carboxylic acids from carbon monoxide and alcohols. The reaction takes place at 250–270° and 200–300 atm. Carbonyl-forming metals with added cuprous chloride or iodine can also be used as catalysts[43]. The

catalytic activity of nickel halides increases considerably in the order: chloride < bromide < iodide. Reaction does not take place in the absence of halides or halogens. The reaction rate and yield of carboxylic acids can be increased by adding to the Co, Ni, and Fe catalysts not only halides or hydrogen halide acids but also polyfunctional compounds such as aminoacetic acid, ethanolamine, *m*-aminophenol, salicylic, tartaric, pyruvic, and adipic acids, or succinodinitrile [44,45]. The reaction can also be carried out in the presence of complexes of Co, Ni, and Fe, for example, $[Co(H_2N-NH_2)_2]I_2$, $[Ni(H_2NCH_2CH_2NH_2)_2]BrI$, $Hg[Co(CO)_4]$, $Ag[Co(CO)_4]$, or compounds of the type Y_2ZX_2, where Y = tetraalkylammonium or triphenylalkylphosphonium ions, Z = Co or Ni, and X = Br or I. [46-50] Advantages of the complex salts relative to simple salts are their stability and ready solubility in the original alcohol and the non-formation of volatile metal carbonyls.

Carboxylic acids are formed more readily from the higher alcohols [43]. The reaction with methanol to give acetic acid takes place with difficulty even at 250–350° and 250–300 atm. Methanol gives only acetic acid, and ethanol gives only propionic acid. Higher alcohols give acids with normal and iso-structures, the latter predominating. Alcohols with high molecular weight give acids with normal structure almost exclusively. The reaction with dihydric alcohols gives dibasic acids:

$$HO(CH_2)_nOH \rightarrow HOOC(CH_2)_nCOOH.$$

These acids in turn can be reduced to dihydric alcohols, which are then used to synthesise $\alpha\omega$-dibasic acids with a longer chain.

Methylglutaric and adipic acids were prepared from butane-1,3-diol. Higher $\alpha\omega$-diols are converted almost exclusively into the corresponding $\alpha\omega$-dibasic acids.

The best catalyst for the reaction is nickel iodide. The use of nickel chloride or bromide leads to side reactions involving the removal of water from the alcohol to yield ethers; the higher alcohols also give alkenes.

Adkins and Rosenthal [51] carried out the reaction in the presence of nickel carbonyl, nickel chloride, hydrochloric acid, and water. Nickel carbonyl and water were taken in excess, but nickel chloride and concentrated hydrochloric acid were taken in "catalytic" quantities. The reaction temperature was 300° for the primary alcohols and 275° for the secondary and tertiary alcohols. Primary alcohols react least readily and give the lowest yield of acids. Primary and secondary aliphatic alcohols with the same number of carbon atoms in the molecule are converted into the same acid with one more carbon atom and a methyl radical in the α-position to the carboxyl group. This was taken as proof that the same α-alkene is formed as intermediate product. Butan-1-ol and butan-2-ol gave α-methylbutyric acid in 47% and 70% yield respectively; heptan-1-ol and heptan-2-ol gave α-methylheptanoic acid in 33% and 70% yield; octan-1-ol and octan-2-ol gave α-methyloctanoic acid in 30% and 76% yield. Pentan-1-ol did not react readily and was converted into α-methylvaleric acid in 16% yield. Neopentanol gave C_6 acids in 21% yield and the tertiary alcohol gave $\alpha\alpha$-dimethylbutyric acid in 35% yield. 2-Ethylbutan-1-ol gave α-methyl-α-ethylbutyric acid in 40% yield. The cyclic alcohols studied were cyclopentanol, 3-cyclohexylpropan-1-ol, 4-methylcyclohexanol, and decahydro-β-naphthol, which were converted into cyclopentanecarboxylic, α-methylcyclohexanepropionic, 4-methylcyclohexanecarboxylic, and decahydronaphthoic acids in 84, 49, 53, and 35% yield respectively. In the case of glycols, one hydroxyl group was carboxylated and the other was reduced. Thus pentane-1,5-diol and hexane-1,6-diol were converted into α-methylvaleric and α-methylhexanoic acids respectively. The hydrogen necessary for the reduction was obtained by the reaction

$$CO+H_2O \rightarrow H_2+CO_2.$$

Aliphatic-aromatic alcohols were converted into alkylbenzenes, again by reduction. 2-(2-Hydroxyethyl)naphthalene gave a resin, apparently as a result of the polymerisation of 2-vinylnaphthalene, the dehydration product of the original alcohol.

The synthesis of carboxylic acids and esters from carbon monoxide and alcohols at 200–300° and 200–400 atm with Ni, Co, and Fe catalysts was studied in detail by Bhattacharyya and coworkers [52-58], who tested a number of Ni and NiI_2 catalysts deposited on silica gel. These showed a high activity. NiI_2 was prepared by precipitating nickel hydroxide from the nitrate with potassium hydroxide and dissolving the precipitate in hydriodic acid.

The maximal yield of acetic acid in the vapour-phase synthesis from methanol was achieved at 180–230°, 260 atm and a concentration of NiI_2 on silica gel equal to 84.2%. After 2 h at 180°, 46% of the methanol was converted into acetic acid, 4% into methyl acetate, and 10% into gaseous products [52,53].

The synthesis of acetic acid from CO and methanol in the vapour phase in the presence of 84.7% $FeI_2.4H_2O$ on silica gel was also studied [59]. The catalyst was found to be highly active. After 2 h at 260 atm and 175°, 11% of the 95% methanol was converted into acetic acid, 4.2% into methyl acetate, and 16.5% into gaseous products. The nickel catalyst gave a smaller quantity of gaseous products and more acetic acid.

The activity of the metals decreases in the order: nickel > cobalt > iron, and that of the halides decreases in the order: iodide > bromide > chloride.

At 210°, an initial pressure of 135 atm, and a contact time of 2 h, nickel, cobalt, and iron, deposited as the metals, chlorides, or bromides on kieselguhr or silica gel, were found to have only low activity. The degree of conversion of methanol into acetic acid was only 0.5–4%. A slightly higher activity was shown by the catalysts FeI_2/SiO_2 (85 : 15) and CoI_2/SiO_2 (84 : 16), with which the degree of conversion at 175° amounted to 8.1% and 16.0% respectively. The highest activity was shown by catalysts containing NiI_2; for NiI_2 without carrier, the degree of conversion was 11.5%. Catalysts consisting of NiI_2 on kieselguhr, pumice, and kaolin, with an NiI_2 : carrier ratio of 70 : 30, gave degrees of conversion equal to 24.0, 21.2, and 14.5% respectively. The addition of CuI, MgO, and ThO_2 reduced the activity.

The best catalyst was found to be NiI_2/SiO_2 (84 : 16), with which the degree of conversion of the methanol was 37%. Under the optimal conditions (265 atm and 200°) on this catalyst, 40% of the methanol was converted into acetic acid. The best cobalt catalyst was CoI_2/SiO_2 (84 : 16), with which the degree of conversion under these conditions was 18.8%. Table 2 gives the equilibrium constants for the reaction [53]:

$$CH_3OH(gas) + CO(gas) \rightarrow CH_3COOH(gas). \quad (3)$$

TABLE 2.

Temperature, °C	Pressure, atm	Equilibrium constant, K_{equil}
25	1	$3.55 \cdot 10^{14}$
150	1	$9.772 \cdot 10^{7}$
210	1	$1.059 \cdot 10^{6}$
250	1	$1.00 \cdot 10^{5}$
400	1	$1.514 \cdot 10^{2}$
300	1	$7.943 \cdot 10^{3}$
300	100	$1.299 \cdot 10^{4}$
300	200	$1.496 \cdot 10^{4}$
300	300	$1.552 \cdot 10^{4}$

Reaction (3) is accompanied by side reactions, including

$$CH_3COOH+CH_3OH \rightarrow CH_3COOCH_3+H_2O,$$
$$CH_3OH \rightarrow CO+2H_2,$$
$$CH_3COOH \rightarrow 2CO+2H_2,$$
$$CH_3COOH \rightarrow CH_4+CO_2,$$
$$CO+H_2O \rightarrow CO_2+H_2,$$
$$CO+3H_2 \rightarrow CH_4+H_2O,$$
$$2CO \rightarrow C+CO_2.$$

Bhattacharyya and coworkers [53] also studied the formation of propionic acid from ethanol and carbon monoxide. At 210°, initial pressure 135 atm, and duration of contact 2 h, Ni, Co, and Fe in the form of the metals, chlorides, or bromides on carriers showed only low activity. The degree of conversion of ethanol into propionic acid was 1.7–4.0%. In the presence of the catalysts CoI_2, NiI_2, and FeI_2 on SiO_2 in the ratio $MI_2/SiO_2 = 85:15$, the degree of conversion at 175° was 14.6, 25.3, and 8.1% respectively. Under the optimal conditions (230° and 280 atm), the degree of conversion on CoI_2 and NiI_2 catalysts was 22.3% and 37.3%.

Table 3 gives values of the equilibrium constant for the reaction

$$CH_3CH_2OH(gas) + CO(gas) \rightarrow CH_3CH_2COOH(gas). \quad (4)$$

The main reaction (4) is accompanied by the side reactions

$$C_2H_5COOH+C_2H_5OH \rightarrow C_2H_5COOC_2H_5+H_2O,$$
$$C_2H_5COOH \rightarrow C_2H_4+CO_2,$$
$$C_2H_5COOH \rightarrow 2CO+H_2+CH_4,$$

and others.

Natta and Pino [60] used nickel carbonyl for the synthesis of acetic acid from carbon monoxide and methanol at 230–250° and 400–600 atm. Up to 0.4 mole of dimethyl ether and 0.2 mole of methyl bromide per mole of methanol were added to the anhydrous reaction mixture. The yield of acetic acid was 66.5%.

TABLE 3.

Temperature, °C	Pressure, atm	Equilibrium constant, K_{equil}
25	1	$1.514 \cdot 10^{11}$
210	1	$5.105 \cdot 10^{2}$
400	1	$1.349 \cdot 10^{-1}$
300	1	3.715
300	100	6.7
300	200	8.0
300	300	8.6

Various cobalt catalysts can be used in the synthesis of saturated acids of low molecular weight and their esters from carbon monoxide and alcohols. Cobalt acetate can be used for the synthesis of acetic acid and methyl acetate [61]. Ethylene bromide and a large excess of dimethylacetamide are added to the reaction mixture. The reaction is carried out at 200–700 atm and 200–250°. The reaction product contains 79% acetic acid and 5% methyl acetate.

The reaction can be carried out to give only the ester. In the reaction of carbon monoxide with methanol at 220° and 650–700 atm in the presence of 2–10% (relative to the alcohol) of cobalt carbonyl, cobalt carbonyl hydride, metallic cobalt, or cobalt oxide, up to 15% methyl acetate is formed in 1 h. [62] The reaction temperature should not exceed 300° to avoid the formation of acetic acid and propionaldehyde. Methyl acetate is obtained under these conditions in the presence of cobalt acetate. The degree of conversion of the methanol is 7% in 0.5 h. Water is also present in the reaction medium. Small quantities of hydrogen increase the reaction rate. The degree of conversion after 0.5 h increases to 25% if the $CO:H_2$ ratio is 3:1. [63] When an alloy with Ni:Co = 17:1 is used as catalyst with the addition of small quantities of NH_4I and BiI_2 (or Bi + I_2), CO and butane-1,4-diol give adipic acid in 45% yield and CO and butyrolactone give glutaric acid [64].

Acetic acid can be synthesised from CO and methanol with a catalyst consisting of a silver halide or its mixture with another metal halide [65] in the presence of water at 300° and 100 atm.

Koch and Haaf [66,67] synthesised carboxylic acids by the reaction of alcohols (or alkenes) with formic acid at atmospheric pressure in the presence of a large excess of concentrated sulphuric acid, which serves both to dehydrate the formic acid and alcohols with the formation of CO and alkenes respectively and also to catalyse the addition of CO to the alkenes. Carbon monoxide adds on according to Markovnikov's rule, and in all cases acids branched in the α-position to the carboxyl group are obtained. The reaction was carried out at room temperature and an alcohol: :formic acid:sulphuric acid molar ratio of 1:2–4:8–12. Thus the reaction medium was kept saturated with carbon monoxide throughout. The reaction product was decomposed with water and the carboxylic acid was extracted from the organic layer produced.

Propanol does not give acids under these conditions, but both n-butanols are converted to α-methylbutyric acid in moderate yield. t-Butanol is converted almost exclusively into trimethylacetic acid in good yield. Pentan-1-ol and pentan-2-ol give 80% yields of a mixture of 80% $\alpha\alpha$-dimethylbutyric acid and 20% of higher acids, chiefly C_{11} acids. 2,3,3-Trimethylbutanol gives $\alpha\alpha\beta\beta$-tetramethylbutyric acid in 90% yield.

$\alpha\alpha$-Dimethylbutyric acid has been synthesised from neopentanol, a 1:2 mixture of $\alpha\alpha$-dimethylvaleric and α-ethyl-α-methylbutyric acids from 2,2-dimethylbutanol, and a 1:2 mixture of $\alpha\alpha$-dimethylhexanoic and α-ethyl--α-methylvaleric acids from 2,2-dimethylpentanol. In these syntheses the yield of acids was 82–85%.

The reaction with cyclopentanol gave a 1.7:1 mixture of cyclopentanecarboxylic acid and the dimeric *cis*-decalincarboxylic acid in 26% yield. Cyclohexanol was converted in 78% yield into a mixture of 78% 1-methylcyclopentanecarboxylic acid, 9% cyclohexanecarboxylic acid, and 13% of C_{13} acids. β-Decalol gives a 1:4 mixture of *trans*- and *cis*-decalincarboxylic acids in 95% yield. An extremely

uniform product is given by primary cyclic alcohols of the neopentanol type. Thus 1-methyl-1-hydroxymethylcyclopentane is converted, with expansion of the ring, exclusively into 1-methylcyclohexanecarboxylic acid in 95% yield. 1-Methyl-1-hydroxymethylcyclohexene and 1-ethyl--1-hydroxymethylcyclohexane react with preservation of the six-membered ring and elongation of the side chain to give 1-ethylcyclohexanecarboxylic and 1-n-propylcyclohexanecarboxylic acid respectively in 86–87% yield.

Carboxylic acids have been synthesised[68,69] by the reaction of an alcohol with carbon monoxide at 50–90 atm and 15–20° in the presence of concentrated sulphuric acid. This synthesis can be regarded formally as the addition of CO to the alcohol with the simultaneous isomerisation of the hydrocarbon radical:

$$ROH+CO \rightarrow R_1COOH,$$

where R_1 is a more highly branched radical than R, with the same number of carbon atoms.

In its first stage, however, this process may involve either dehydration of the alcohol to the alkene:

$$RCH_2CH_2OH \rightarrow RCH{=}CH_2+H_2O,$$

which then reacts according to the schemes:

$$R_1R_2C{=}CR_3R_4+H_2SO_4 \rightarrow R_1R_2HC{-}\overset{+}{C}R_3R_4+\overline{O}SO_3H \xrightarrow{CO}$$

$$\xrightarrow{CO} R_1R_2HC{-}CR_3R_4\overset{+}{C}O + \overline{O}SO_3H \rightleftarrows \underset{\text{(I)}}{R_1R_2HCR_3R_4C{-}COSO_3H} \quad \underset{\text{(II)}}{\parallel O}$$

or

$$\text{(I) [or (II)]} + HX \longrightarrow R_1R_2HC{-}R_3R_4C{-}\underset{\parallel O}{C}{-}X,$$

or direct conversion of the alcohol into the carbonium ion, according to the reaction

$$RCH_2CH_2OH + H_2SO_4 \longrightarrow RCH_2\overset{+}{C}H_2 + \overline{O}SO_3H + H_2O.$$

The second direction is more probable. This is confirmed by the preparation of carboxylic acids from alcohols of the neopentanol type, which cannot be dehydrated directly to alkenes[67].

The synthesis of the acids and their esters was carried out in such a way that the alcohol, CO, and sulphuric acid reacted in the first stage, and in the second stage an excess of water or methanol was added to the reaction mixture. In the first case, carboxylic acids were obtained, and in the second case their methyl esters, with traces of the carboxylic acids themselves, were obtained. The total yield of esters and acids from the aliphatic C_3–C_5 alcohols increased with increase in the molecular weight of the alcohol and reached 85%. Alcohols with the iso-structure reacted more readily than those with normal structure and the same molecular weight. The yield of esters and acids from the aliphatic C_6–C_9 alcohols was approximately on the same level (76–82%), irrespective of the molecular weight. The yield of esters and acids from the cyclic alcohols (cyclohexanol and menthol) reached 91–94%.

The following acids and their esters were obtained as the chief reaction products: isobutyric acid from propanol and isopropanol, α-methylbutyric acid from n-butanol, trimethylacetic acid from isobutanol, αα-dimethylbutyric and α-ethylbutyric acids (in the ratio 1.7 : 1) from n-pentanol, αα-dimethylbutyric acid from isopentanol, αα-dimethylvaleric and α-ethylvaleric acids from n-hexanol, αα-dimethylhexanoic and α-ethylhexanoic acids from n-heptanol, αα-dimethyloctanoic acid from n-nonanol, 1-methylcyclopentane-1-carboxylic and cyclohexanecarboxylic acids from cyclohexanol, and menthanecarboxylic acid (4-isopropyl-1--methylcyclohexane-3-carboxylic acid) from menthol.

The data in this section show that the reaction of carbon monoxide with alcohols may take place in three different directions, with the formation of formates, carboxylic acids, and esters respectively. Formates are produced in the presence of alkali metal alkoxides at increased temperature (100–300°) and high pressure (200–1000 atm). The synthesis of carboxylic acids and their esters is carried out at about the same temperatures and pressures in the presence of cobalt, nickel, and iron catalysts or acidic catalysts (phosphoric acid and boron trifluoride). In the presence of concentrated sulphuric acid the synthesis can be carried out at room temperature and a pressure of 50–90 atm, in two stages. In the first stage, the alcohol, CO, and sulphuric acid react, and in the second stage an excess of water or methanol is added to give the corresponding carboxylic acids or their esters.

3. REACTIONS OF CARBON MONOXIDE WITH ALKENES AND WATER

In a study of the reaction of carbon monoxide with alcohols, Hardy[35] suggested that the alcohols are first dehydrated to alkenes, which then react with carbon monoxide and water to form carboxylic acids. This he confirmed experimentally by preparing carboxylic acids from alkenes, carbon monoxide, and water at 200–300° and 150–200 atm in the presence of 87% phosphoric acid[70].

The synthesis of carboxylic acids from alkenes, carbon monoxide, and water at 130–375° and pressures up to 700 atm was described in a number of patents. The catalysts used were phosphoric, boric, arsenic[71], and monochloroacetic acids, acetyl chloride on active carbon[72], and Ba and Ca halides[73]. Boron trifluoride is often used[74]. 2,2,3-Trimethylbutyric acid was prepared in quantitative yield from tetramethylethylene and CO at 75–77° and 400 atm in the presence of $BF_3.3H_2O$.[75] Ethyl αα-dimethylbutyrate was prepared from ethylene, propene, and CO at 110° and pressures up to 900 atm in the presence of BF_3.[76] Ethyl α-ethyl-α-methylbutyrate was prepared from a 3 : 5 mixture of C_2H_4 and CO in the presence of $BF_3.1.7H_2O$ under the same conditions[77].

Compounds of general formula $RR_1C{=}CR'CH_2X$, where R may be a hydrogen atom, a C_1–C_6 alkyl group, or the phenyl group, and R' an alkyl or phenyl group (but not H, since in this case no reaction occurs) and X a halogen, react with CO at 60–150° and 200–2000 atm in the presence of $BF_3.2H_2O$ to give αα-dialkyl-β-halogenopropionic acids[78]. Dibasic carboxylic acids and their esters are obtained by the reaction of aliphatic unsaturated monocarboxylic acids and their esters with CO and water at 75–300° and 400–1000 atm in the presence of BF_3. The original acid : BF_3 : : water ratio was 3 : 1 : 3. In the molecule of the original acid the double bond should be separated from the carboxyl group by at least two carbon atoms[32].

In the synthesis of carboxylic acids from alkenes, CO, and water, the catalysts used are the carboxylic acids which should be formed during the reaction, or others[79]. Ethylene, CO, and water in the ratio 0.9 : 1 : 2 at 290° and initial pressure 133 atm in the presence of propionic acid gave the same acid in 71% yield.

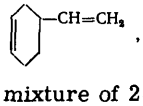
Nickel and cobalt carbonyls and nickel and cobalt salts which are converted into carbonyls during the reaction have been widely used as catalysts in the reaction of alkenes with CO and water. The use of finely divided metallic nickel as a catalyst for this reaction was reported as early as 1934.[80]

In 1940, the method developed by Reppe and coworkers for the carboxylation of acetylenic compounds in the presence of nickel carbonyl and nickel salts was extended to olefinic compounds in order to obtain saturated carboxylic acids and their derivatives[42]. The catalyst used in these reactions was nickel carbonyl. The starting materials in the reactions were alkenes and their functional derivatives — unsaturated alcohols, acids, etc.[81] The carboxylation of the olefinic compounds, like that of the acetylenic compounds[82], can be carried out either with stoichiometric quantities of nickel carbonyl in the presence of the acid necessary to dissolve the nickel, in which case the carbonyl acts as the source of CO (method A), or by using CO and "catalytic" quantities of nickel carbonyl, nickel salts, or metallic nickel (method B). The alkene and the compound with the labile hydrogen react simultaneously. The reaction takes place at higher temperatures and pressures than in the case of the acetylenic compounds, namely 100–200 atm and 160–190° in method A and 230–285° in method B. The high pressures in method B make it possible to avoid the addition of acid to combine with the nickel, since under these conditions the metal forms nickel carbonyl.

The reaction products are saturated carboxylic acids or their derivatives. The resulting acid may be converted into the anhydride by the further action of the alkene and CO:

$$CH_3CH_2COOH + CO + H_2C{=}CH_2 \longrightarrow (CH_3CH_2CO)_2O.$$

Branched acids, chiefly α-methyl-substituted acids, are formed in addition to acids with the normal structure. Propionic acid and its anhydride were obtained in a smooth reaction from ethylene. Propene was converted into a mixture of approximately equal quantities of butyric and isobutyric acids; isobutene into a mixture of isovaleric acid and a trace of trimethylacetic acid; and 2-ethylhex-1-ene into a mixture of 2-ethyl-2-methylhexanoic and 3-ethylheptanoic acids. Cyclohexene, cyclooctene, and octadec-1-ene gave cyclohexanecarboxylic, cyclooctanecarboxylic, and α-methylstearic acids respectively. Buta-1,3-diene, by diene synthesis, gave 1-vinylcyclohex-3-ene

$$CH_2{=}CH{-}CH{=}CH_2 + CH_2{=}CH{-}CH{=}CH_2 \longrightarrow \text{  },$$

which was subsequently converted into a mixture of 2- and 3-vinylcyclohexanecarboxylic and α- and β-(cyclohex-3-enyl)propionic acids. Under the more severe conditions of method B (CO + nickel carbonyl), a mixture of dicarboxylic acids, namely α- and β-(3- and 4-carboxycyclohexyl)propionic acids, was formed. Biallyl gave 2- and 3-methyl-4-vinylbutyric acids and the corresponding dicarboxylic acids. An attempt to carboxylate styrene did not give satisfactory results, since the acid polymerised under these conditions. Unsaturated alcohols were converted into hydroxy-acids, hemi-esters, and lactones. Allyl alcohol, however, gave crotonic acid (apparently by dehydration of the initial γ-hydroxybutyric acid), the lactone, and a polymer of methacrylic acid. Carboxylation of unsaturated carboxylic acids containing a double bond gave saturated dicarboxylic acids and their derivatives. Oleic acid gave a mixture of heptadecane-1,8-dicarboxylic and heptadecane-1,9-dicarboxylic acids and small quantities of hydroxystearic acid.

In the case of the reaction in the liquid phase, inert liquids (aromatic and naphthenic hydrocarbons, ketones) are used[83] and in the case of the reaction in the gaseous phase, carbon dioxide is used as diluent and also serves to suppress the water–gas reaction. Under these conditions, at 300–375° and 450–740 atm in the presence of nickel carbonyl, ethylene gave a 40% yield of propionic acid, and propene gave a 76% yield of butyric and isobutyric acids in the ratio 2 : 1.

4-Methyloctanoic acid was obtained in 33% yield from oct-1-ene at 300° and 300 atm in the presence of a catalyst containing 65% nickel carbonyl, 10% nickel chloride, and 25% hydrochloric acid[84].

The reaction takes place more rapidly and with higher yields of acids in the presence of an Ni catalyst promoted with HI.[85] At 300° and 400 atm in the presence of nickel acetate, hex-1-ene reacts with CO and water more slowly than pent-1-ene; pent-2-ene reacts even more slowly and 2-methylbut-2-ene does not react at all. If 0.013 mole of HI per 1–1.5 mole of alkene is added to the nickel catalyst, the rate of carboxylation of pent-1-ene, pent-2-ene, and hex-1-ene is increased by a factor of 40, but the rate of reaction of 2-methylbut-2-ene is only one-half of this value. The total yield of acids reaches 90%. Pent-1-ene and pent-2-ene both gave hexanoic and 2-methylvaleric acids, hex-1-ene gave a mixture of heptanoic and 2-methylhexanoic acids, and 2-methylbut-2-ene gave a mixture of at least three acids: 3-methylvaleric, 4-methylvaleric, and 2,3-dimethylvaleric acids. In the presence of an unpromoted catalyst, pent-1-ene and hex-1-ene gave products containing 40% of straight-chain acids and 60% of branched-chain acids; the corresponding figures for pent-2-ene were 30% and 70% respectively. With a promoted catalyst, the quantity of straight-chain acids increased to 47% and 44% respectively.

Cobalt-based catalysts have also been widely used in this reaction. Propionic acid was prepared from ethylene, CO, and water at 270–290° and 300–600 atm in the presence of cobalt carbonyl[86]. At 285° and 200 atm the yield was 85%.[87,88]

Ercoli[89] studied the conditions for the synthesis of carboxylic acids from alkenes, CO, and water in the presence of $Co_2(CO)_8$. The use of solvents decreases the reaction temperature to 120–125° and the pressure to 100–300 atm. The yield of acids reaches 80–90%. The ease of reaction decreases with increased extent of branching of the original alkene. The cobalt catalyst, however, tends to produce side reactions; for example, considerable quantities of diethyl ketone are formed in the carboxylation of ethylene[83].

The rate of carboxylation of cyclohexene in the presence of cobalt octacarbonyl is proportional to the water concentration and to the square root of the cycloalkene concentration. The maximal reaction rate at 156° is achieved at 165–210 atm. At lower pressures the rate of reaction is directly proportional to the pressure, and at higher pressures (above 340 atm) the reaction rate is inversely proportional to the pressure. The reaction rate increases with increase in the Co concentration[90].

Propionic acid was synthesised in 50–85% yield in the presence of cobalt propionate or butyrate in aqueous

medium at 200–250°, 135–270 atm and $C_2H_4 : CO = 1 : 3$. Diethyl ketone and CO_2 are formed in side reactions. The catalyst is deactivated when the reaction medium contains more than 28% CO_2.[91] Propionic acid was obtained in 55% yield from ethylene, CO, and water in the presence of cobalt formate in aqueous trimethylamine solution at 220° and 300 atm.[92] Propionic acid was prepared from a 1 : 1 mixture of C_2H_4 and CO at 180° and 340 atm in the vapour phase on a $Co-Fe-ThO_2-MgO$-kieselguhr (30 : 1 : 2 : 2 : 65) catalyst reduced in a current of H_2 at 400°; the degree of conversion after 3 h was 10–13%.[93] In the presence of CoI_2/SiO_2 and NiI_2/SiO_2 (50 : 50) at 230–300° and 300 atm the yield of this acid after 3 h was 7.3% and 27.9% respectively[54]. The main reaction

$$C_2H_4 + CO + H_2O \longrightarrow C_2H_5COOH,$$

was accompanied by a number of side reactions, including

$$n\,C_2H_4 \longrightarrow (C_2H_4)_n,$$

$$C_2H_4 \longrightarrow 2C + 2H_2,$$

$$C_2H_4 \longrightarrow C + CH_4,$$

$$C_2H_4 + CO + H_2 \longrightarrow C_2H_5CHO.$$

Polyethylene is formed on catalysts subject to prolonged reduction.

Carboxylic acids can also be synthesised from alkenes and CO in the presence of aqueous solutions of iron salts[94].

These data show that the single-stage synthesis of carboxylic acids from alkenes, CO, and water when all the original reagents are present in the reaction mixture requires the use of increased temperatures (100–350°) and high pressure (200–1000 atm).

A new development was the two-stage synthesis of carboxylic acids, carried out in 1955 by Koch[95,96]. In the first stage, the alkene reacted with CO in the presence of 96% sulphuric acid, and in the second stage, decomposition of the reaction complex with water gave the carboxylic acid. The acids were obtained in good yield under very mild conditions at 0–50° and 1–100 atm with vigorous stirring. The reaction usually obeys Markovnikov's rule. Propene was converted only into isobutyric acid, but-1-ene and but-2-ene into α-methylbutyric acid, and isobutene chiefly into trimethylacetic acid. Increase in pressure retards the polymerisation of the alkenes and the isomerisation of the carbon chain. Pent-2-ene at 5 atm was converted in 59% yield into a mixture of approximately equal quantities of C_6, C_{11}, C_{16}, and C_{21} acids, the only C_6 acid being αα-dimethylbutyric acid. At 100 atm, pent-2-ene gave a 70% yield of a mixture of α-methylvaleric and α-ethylbutyric acids with a small quantity of αα-dimethylbutyric and higher acids. The same acids were formed from pent-1-ene. The three n-hexenes gave four isomeric C_7 acids; α-methylhexanoic, αα-dimethylvaleric, α-ethylvaleric, and α-ethyl-α-methylbutyric. These acids were also obtained from 2-methylpent-1-ene, 2-ethylbut-1-ene, and 3-methylpent-2-ene, but ααβ-trimethylbutyric acid was obtained from 2,3-dimethylbut-2-ene and 2,3-dimethylbut-1-ene. "Diisobutylene" and "triisobutylene" gave 2,2,4,4-tetramethylvaleric and methyldineopentylacetic acids respectively. It was subsequently shown that in the presence of a large excess of sulphuric acid CO can be replaced by formic acid, and in this case the reaction takes place at atmospheric pressure[66]. When this method was used, pent-2-ene gave a mixture of acids containing 80% αα-dimethylbutyric acid and 16% of dimeric C_{11} acids; hex-1-ene gave αα-dimethyl valeric, α-ethyl-α-methylbutyric and dimeric C_{13} acids; and dec-1-ene gave exclusively C_{11} acids, chiefly tertiary acids, in 84% yield. In the product obtained from branched alkenes, the acid with one carbon atom more than the original alkene is not the chief component and the mixture obtained contains all the isomers of the dimeric acids, together with acids containing a different number of carbon atoms.

The original alkene can be replaced by an alcohol or alkyl chloride[68-69].

An extremely interesting development of this method established the possibility of synthesising carboxylic acids from paraffins under conditions of acid catalysis[97]. Mixtures of an alkene (or alcohol) with an isoalkane (or cycloalkane) with the addition of formic acid or an excess of sulphuric acid gave, in addition to the expected acids, other acids derived from the saturated hydrocarbon. This reaction can be attributed to the transfer of a hydride ion from the isoalkane or cycloalkane to the carbonium ion formed by the reaction of the alkene with sulphuric acid. Thus the saturated hydrocarbon forms a new carbonium ion which reacts further with carbon monoxide and water to give carboxylic acids. Thus t-butanol and isopentane give αα-dimethylbutyric acid in addition to trimethylacetic acid. The yield of exchange acid reaches 74%. The yield of exchange acid decreases with increase in the chain length of the isoalkane and increase in the distance between the branching and the end of the straight chain. Cycloalkanes containing no side-chain give carboxylic acids with a smaller ring: cyclohexane gives 1-methylcyclopentane-1-carboxylic acid, cycloheptane gives 1-methylcyclohexane-1-carboxylic acid, and cyclooctane gives 1-ethylcyclohexane-1-carboxylic acid. The synthesis of carboxylic acids from alkanes by the hydride migration method can also be brought about by the reaction with carbon monoxide under pressure in the presence of a large excess of sulphuric acid. Favourable reaction conditions can be selected using the fact that the carbonium ion initially formed from the alkene may react further in two ways: by the direct addition of carbon monoxide or by an exchange reaction with alkanes. Only the former is facilitated by high pressure, so that the synthesis of the exchange acids takes place only at pressures below 20 atm. For example, the maximum yield of acids (52%) in the synthesis from propene–methylcyclopentane vapour is achieved at a pressure of 5 atm.

The data in this section show that the reaction of carbon monoxide with alkenes and water takes place with the formation of the carboxylic acids and esters which are produced in the reaction of carbon monoxide with the corresponding alcohols. The two reactions take place in the presence of the same catalysts — cobalt, nickel, and iron compounds, phosphoric acid, and boron trifluoride — and under approximately the same conditions — at increased temperature (100–350°) and high pressure (200–1000 atm). The reaction can also be carried out in two stages and under very mild conditions (0–50°, 1–100 atm) with high yield of carboxylic acids in the presence of acidic catalysts, particularly sulphuric acid. In the first stage the alkene and carbon monoxide react with the catalyst and in the second stage the third component — water — is introduced.

4. REACTIONS OF ALCOHOLS AND ALKENES WITH CARBON MONOXIDE

When the formation of carboxylic acids from alkenes and carbon monoxide takes place in the presence of alcohols,

esters may predominate in the reaction products. Thus the reaction of alkenes, alcohols, and CO over active carbon impregnated with phosphoric acid gave a mixture of carboxylic acid, esters, and ethers[98]. Reppe and coworkers[82] synthesised esters from alkenes, alcohols, and CO in the presence of carbonyl-forming metals or their derivatives. The reactions were carried out at 100–200 atm and 160–190° with stoichiometric quantities of $Ni(CO)_4$ (method A) and at 270–285° with CO and "catalytic" quantities of the Ni compounds (method B). Activators, for example mineral acids, which increase the yield of esters, may also be used. Ethyl isononanate was obtained in up to 95% yield in the liquid phase using inert solvents in the presence of NiI_2 and acetic acid. Ethylene, CO, and butanol in the presence of small quantities of propionic acid and $Ni(CO)_4$ gave butyl propionate in 72% yield. 12% of propionic anhydride was formed simultaneously[99,100]. In the presence of Ni halides the main reaction is accompanied by a number of side reactions, such as esterification, trans-esterification, ester hydrolysis, and carboxylation. Higher acids and polyalkenes are also formed. The hydrogen produced by the water–gas reaction does not hydrogenate the alkene but is consumed in the formylation of the alkene to aldehydes and hydrogenation of the latter to alcohols.

Natta, Pino, and their coworkers[101,102], in the synthesis of esters from alkenes, carbon monoxide, and alcohols, made extensive use of catalysts based on cobalt. Their experience with the carboxylation of acetylene to acrylates was applied to the reaction with alkenes, cycloalkenes, and polyalkenes. They used metallic cobalt deposited on diatomite. The reaction was carried out at 100–200° and 10–200 atm. Cyclohexene, CO, and an excess of methanol gave methyl cyclohexanecarboxylate in 76–86% yield[103]. Small quantities of hexahydrobenzaldehyde were formed in the side reaction

$$C_6H_{10} + CO + H_2 \longrightarrow C_6H_{11}CHO.$$

Under the same conditions, cyclohexene, CO, and a small excess of butanol gave a mixture of hexahydrobenzyl butyrate, butyl hexahydrobenzoate, hexahydrobenzyl, hexahydrobenzoate, butyl butyrate, hexahydrobenzyl alcohol, methyl hexahydrobenzoate, and hexahydrobenzaldehyde[104]. Methyl crotonate, methanol, and CO at 192 atm and 200° gave methyl methylsuccinate containing a little β-formylbutyric acid. Butyl crotonate, butanol, and CO gave butyl methylsuccinate in 70–79% yield. Butyl butyrate and β-formylbutyrate were formed in side reactions. Butene, CO, and methanol gave methyl valerate in 25% yield[105]. Esters of propionic, butyric, and isobutyric acids were synthesised in analogous fashion. The yield of esters when methanol was used was much greater than that for higher alcohols, since side reactions play a smaller part. The thermodynamic conditions for the carboxylation reaction are evidently more favourable than those for carbonylation (the oxo-process), but in practice the carboxylation takes place more slowly because of kinetic factors[103,106]. The cobalt salts of carboxylic acids were used as catalysts[105]. On these catalysts a ternary mixture of CO, alkenes, and secondary alcohols reacts to form ketones. CO, ethylene, and isopropanol in the presence of cobalt butyrate and cobalt(II) oxide gave acetone and diethyl ketone in quantitative yield. In analogous fashion, ethylene and cyclohexanol gave diethyl ketone and cyclohexanol in 70% yield. The reaction takes place at 225–300° and 600–750 atm.[107]

The reaction of cyclohexene with CO and a large excess of methanol at 165° and 60–390 atm in the presence of $Co_2(CO)_8$ gives methyl cyclohexanecarboxylate containing the dimethylacetal of hexahydrobenzaldehyde. The formation of the acetal is favoured by a low molar alcohol : alkene ratio, a high concentration of Co salt solution, low CO pressure, and high temperature. The reaction is of zero order with respect to alkene and first order with respect to methanol. Its rate passes through a maximum at a pressure of 60–90 atm.[108]

Bhattacharyya and coworkers[54] used CoI_2, NiI_2, and FeI_2 deposited on SiO_2 in the ratio 50 : 50. At 300 atm and 230–300°, ethylene, CO, and methanol gave methyl propionate in yields of 26.0, 20.0, and 27.1% respectively. Ethyl propionate was obtained in yields of 25.1, 24.4, and 23.5% when methanol was replaced by ethanol. Table 4 gives the equilibrium constants for the reaction

$$C_2H_4(gas) + CO(gas) + CH_3CH_2OH(gas) \rightarrow CH_3CH_2COOC_2H_5(gas).$$

The reaction between alkenes, CO, and alcohols can be carried out at 80–200° and 600–1000 atm in the presence of the alcohol-soluble salts of the noble metals of Group VIII (Pt, Pd, Rh, and Ir) and the alcohol-soluble salts of tin and germanium. Under these conditions, ethylene, CO, and methanol, ethanol, isopropanol, butanol, or cyclohexanol gave respectively methyl, ethyl, isopropyl, butyl, and cyclohexyl propionates. In analogous fashion allene or allylene, CO, and methanol gave methyl methacrylate, and *cis*-but-2-ene, CO, and methanol gave methyl α-methylbutyrate[109].

Thus the synthesis of the esters of carboxylic acids, like that of the carboxylic acids themselves, takes place under severe conditions and requires the use of increased temperature and high pressure. In 1958 the authors of the present paper achieved a two-stage synthesis of the esters of carboxylic acids under much milder conditions at 20–40° and 20–80 atm.[110–118]

Solutions of carboxylic acids in concentrated sulphuric acid readily esterify methanol[119]. It is suggested that the reaction of carboxylic acids with sulphuric acid gives acylsulphuric acids which react with methanol to give esters. Koch[67,95,96] obtained carboxylic acids by using water to decompose a reaction mixture formed from alkenes and CO in the presence of concentrated sulphuric acid. After a comparison of these results and an analysis of the possible nature of the reactive complex from CO, an alkene and sulphuric acid, we suggested that in this case acylsulphuric acids should be formed. These may be present in equilibrium with acylinium ions:

$$R_1R_2C{=}CR_3R_4 + H_2SO_4 \longrightarrow R_1R_2HC{-}\overset{+}{C}R_3R_4 + \overline{O}SO_3H \xrightarrow{CO}$$

$$\xrightarrow{CO} \underset{(III)}{R_1R_2HC{-}C(R_3R_4)\overset{+}{C}O} + \overline{O}SO_3H \rightleftarrows \underset{(IV)}{R_1R_2HC{-}C(R_3R_4)CO{-}OSO_3H}.$$

TABLE 4.

Temperature, °C	Pressure, atm	Equilibrium constant, K_{equil}
25	1	$1.135 \cdot 10^{15}$
100	1	$6.86 \cdot 10^{8}$
200	1	$4.06 \cdot 10^{3}$
300	1	1.610
230	1	$2.79 \cdot 10^{2}$
230	100	$4.378 \cdot 10^{2}$
230	200	$4.639 \cdot 10^{2}$
230	250	$4.64 \cdot 10^{2}$

Forms (III) and (IV) should exhibit acylating properties and should convert compounds with labile hydrogen into derivatives of carboxylic acids:

$$\text{(III) [or (IV)]} + HX \longrightarrow H_2SO_4 + R_1R_2HC{-}R_3R_4C{-}\underset{\underset{O}{\|}}{C}X.$$

In the particular case where X = OH, they should give carboxylic acids according to Koch's reaction. When X = OR, *i.e.* with alcohols, forms (III) and (IV) should be converted into esters, as confirmed in our experiments. The reaction of the complex formed from an alkene, CO, and sulphuric acid with methanol or ethanol gave the corresponding esters. The yield of esters was 60–85% relative to the original alkene, or 70–100% relative to the CO absorbed. The starting materials in the carbalkoxylation reaction were C_4–C_{10} α-alkenes with normal structure, isobutene, all the isomeric pentenes, and the cycloalkenes: cyclopentene, cyclohexene, and dihydrodicyclopentadiene. The chief reaction product from α-alkenes with normal structure are the esters of $\alpha\alpha$-dimethylalkanoic acids with one carbon atom more than the original alkene. But-1-ene gave α-methylbutyrate, isobutene gave trimethylacetate, pent-1-ene, hex-1-ene, hept-1-ene, oct-1-ene, non-1-ene, and dec-1-ene gave $\alpha\alpha$-dimethylbutyrate, $\alpha\alpha$-dimethylvalerate, $\alpha\alpha$-dimethylhexanoate, $\alpha\alpha$-dimethylheptanoate, $\alpha\alpha$-dimethyloctanoate, and $\alpha\alpha$-dimethylnonanoate. The isomeric pentenes gave chiefly $\alpha\alpha$-dimethylbutyrate; cyclopentene gave esters of cyclopentanecarboxylic and *cis*-decalin-9-carboxylic acids, cyclohexene gave esters of 1-methylcyclopentanecarboxylic and cyclohexane carboxylic acids in almost equal quantities. Dihydrodicyclopentadiene gave the ester of 4,7-endomethylenehydrindancarboxylic acid.

In the synthesis of esters of carboxylic acid from CO, alcohols, and alkenes in the presence of sulphuric acid, as in the case of the synthesis of the carboxylic acids themselves from alkenes, CO, and water (see p. 443), saturated hydrocarbons may take part in the reaction as a result of the hydride transfer process. In this case the starting materials are mixtures of alkanes or cycloalkanes with alkenes or alcohols. The carbonium ions formed in the first stage from the alkenes or alcohols combine with the hydride ions produced from the alkanes or cycloalkanes containing hydrogen or a tertiary carbon atom. The latter give up hydride ions and are converted into carbonium ions. Thus in the first stage, carbonium ions are produced from the alkanes and these add on CO and are converted into acylinium ions. In the second stage, methanol is added and this reacts with the acylcarbonium ions to form the methyl esters of carboxylic acids.

The hydride ion transfer reaction proceeded to the greatest extent in isopentane–t-butanol vapour; in this case 93% yield of the esters was obtained from isopentane and only 7% from t-butanol. The ratio of the esters obtained by exchange and direct synthesis from isopentane–menthol vapour was 1 : 1, that from isopentane–cyclohexane vapour 1 : 1.3–1.5, and that for isopentane–isononene vapour 1 : 2.2. Methylcyclohexane underwent the hydride transfer reaction with t-butanol, triisobutene, cyclohexene, and isononenes to the extent of 80, 73, 50, and 24% respectively. The hydride transfer reaction does not take place between n-hexane and t-butanol, cyclohexene, or isononenes, evidently because there is no hydrogen on the tertiary carbon atom.

Thus the simultaneous reaction of carbon monoxide with alkenes and alcohols gives esters of carboxylic acids containing some of the carboxylic acids themselves.

The formation of the esters of carboxylic acids takes place under the same conditions and on the same catalysts as the reaction of carbon monoxide with alcohols and the reaction of carbon monoxide with alkenes and water.

5. MECHANISM OF CARBOXYLATION REACTIONS

In carboxylation by means of carbon monoxide and particularly in the synthesis of acids and esters by this method, the catalysts used are mineral acids, particularly phosphoric and sulphuric acids, their salts (phosphates), BF_3, the metals Co, Ni, and Fe in the reduced state, and their oxides, halides, and carbonyls. The mechanism of the carboxylation naturally depends to a considerable extent on the catalyst used.

According to Hardy [41], in the synthesis of carboxylic acids from alkenes, CO, and water in the presence of concentrated phosphoric acid, the alkene molecule is first activated by the formation and subsequent decomposition of alkyl phosphates. The activated alkene molecules then add on CO with the formation of complexes which react with water to give carboxylic acids.

For the reaction in the presence of $BF_3 . 1.7H_2O$ the following ionic scheme has been assumed [77]:

$$C_2H_4 + \overset{+}{H} \longrightarrow CH_3\overset{+}{C}H_2 \xrightarrow{C_2H_4} CH_3CH_2CH_2\overset{+}{C}H_2 \rightleftarrows CH_3CH_2CH_2\overset{+}{C}H_2 \xrightleftharpoons{C_2H_4}$$

$$\xrightleftharpoons{C_2H_4} CH_3CH_2\underset{\underset{CH_3}{|}}{\overset{+}{C}H}CH_2CH_3 \rightleftarrows CH_3CH_2\underset{\underset{CH_3}{|}}{\overset{+}{C}H}CH_2CH_3 \rightleftarrows CH_3CH_2\underset{\underset{CH_3}{|}}{CH}\overset{+}{C}H_2 \xrightarrow{CO}$$

$$\xrightarrow{CO} (CH_3CH_2)_2\underset{\underset{CH_3}{|}}{C}\overset{+}{C}O \xrightarrow[-\overset{+}{H}]{H_2O} (C_2H_5)_2\underset{\underset{CH_3}{|}}{C}COOH \xrightarrow{C_2H_4} (C_2H_5)_2\underset{\underset{CH_3}{|}}{C}COOC_2H_5.$$

The tendency of primary and secondary carbonium ions to undergo conversion into tertiary ions is evidently extremely high, since no products corresponding to the intermediate ions were obtained.

In a discussion of the mechanism of the carboxylation of acetylene in the presence of nickel carbonyl, Reppe [82] considers the possibility that the CO reacts with the iso-form of acetylene with the intermediate formation of methyleneketen which subsequently can react readily with water or alcohol to give acrylic acid or its esters:

$$H_2C{=}C{+}CO \longrightarrow (H_2C{=}C{=}CO) \xrightarrow[ROH]{H_2O} \begin{matrix} H_2C{=}CHCOOH \\ H_2C{=}CHCOOR \end{matrix}.$$

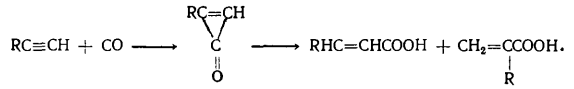
The keten scheme cannot, however, explain either the reactivity of symmetrically disubstituted acetylenes or the formation of two reaction products. The ester of cinnamic acid, which should be the only reaction product formed according to this scheme from phenylacetylene, CO, and alcohol:

$$C_6H_5C{\equiv}CH + CO \longrightarrow \begin{matrix} H_5C_6 \\ H \end{matrix}\!\!>\!C{=}C{-}CO \xrightarrow{ROH} \begin{matrix} H_5C_6 \\ H \end{matrix}\!\!>\!C{=}CHCOOR$$

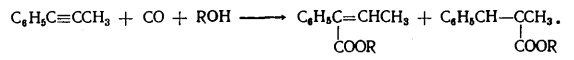
is not formed, the product being the ester of α-phenylacrylic acid.

It was therefore suggested [120,121] that the carboxylation, like the carbonylation of alkenes (the oxo-process), involves the formation of an intermediate hypothetical cyclopropene

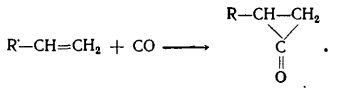
ring from acetylene and CO, and that this opens under the influence of compounds with a labile hydrogen atom:



If molecular hydrogen is used instead of a compound with labile hydrogen, the reaction does not give satisfactory results. It can be seen from this scheme that two products should in general be formed. In actual fact, methylphenylacetylene, for example, gives two esters: α-phenylcrotonate and α-phenylcinnamate:



In the carboxylation of alkenes an intermediate cyclopropanone derivative is formed instead of the cyclopropenone derivative:

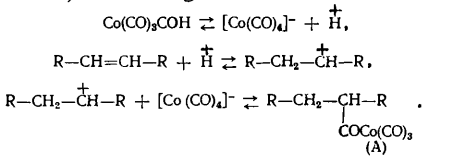


Ghis gives aldehydes with H_2, acids with water, and esters with alcohols, and in this case also the formation of two derivatives is possible.

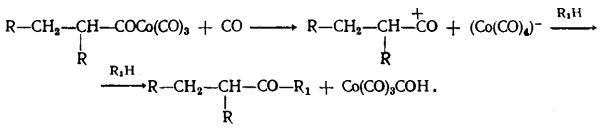
Doubts have been cast on this mechanism[122]. It has been pointed out that the formation of cyclopropanone derivatives should not be related to the presence of compounds with labile hydrogen. At the same time, in the absence of such a compound, these cyclic derivatives are never formed. Moreover, the reversibility of the oxo-process is not in accordance with the properties of derivatives with a saturated three-membered carbon ring. Another mechanism was therefore proposed[122], according to which the reagent with labile hydrogen reacts with the metal carbonyl catalyst to give intermediate compounds which in turn react with alkenes to form new intermediate compounds in which one carbon atom in the alkene is joined directly to the central atom of the metal carbonyl. This mechanism explains the difference in the reaction rates when different compounds with labile hydrogen are used, but it cannot explain the difference in the behaviour of nickel and cobalt in the synthesis of esters.

When it was suggested[123] that cobalt carbonyl hydride $Co(CO)_3COH$ [hydrogen tetracarbonylcobaltate(I) (Ed. of Translation)] is formed as an intermediate product in the oxo-process and it was pointed out[124] that the reaction of cobalt carbonyl with CO precedes its reaction with a reagent containing labile hydrogen, Natta and Pino[104] suggested a new mechanism for the carboxylation of alkenes with carbon monoxide in the presence of a catalyst based on metallic cobalt. According to their scheme, the active catalyst, as in the case of carbonylation reactions (the oxo-process), is an intermediate cobalt carbonyl hydride $Co(CO)_3COH$. This adds on to the double bond of the alkene to form an intermediate compound which then reacts with the compound containing labile hydrogen.

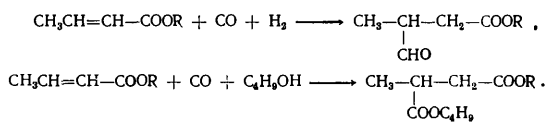
Cobalt carbonyl hydride exhibits the properties of a strong acid. It may therefore be assumed that it adds on to alkenes in the same way as hydrochloric, sulphuric, and similar acids, according to the scheme:



The compound (A) has a low stability and reacts with a CO molecule to form the $[Co(CO)_4]^-$ ion and an active carbonium ion, which rapidly reacts with the compound containing active hydrogen to regenerate cobalt carbonyl hydride:



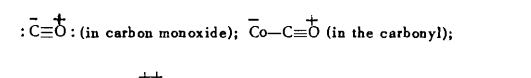
Natta and Pino[104] put forward some evidence in support of this mechanism. They point out that as a result of the part played by cobalt carbonyl hydride, aldehydes are formed, both in the oxo-process and in the carboxylation reaction. This is a stage common to both reactions. In both cases, when the reactions are carried out with esters of crotonic acid, only one reaction product is obtained, in which the formyl or carbalkoxy-groups respectively are found in the β-position:



α-Formyl butyrate is not formed in the oxo-process, and ethyl malonate is not formed in the carboxylation process. This also confirms the analogy between the mechanisms of the two reactions.

The formation of cobalt carbonyl hydride does not require the presence of large quantities of hydrogen, and small quantities of water or hydrogen sulphide are sufficient[125]. In the synthesis of esters, water is formed by the dehydration of the alcohols to ethers and hydrogen is formed by the dehydrogenation of the alcohols to aldehydes. This is confirmed by the presence, in the reaction products, of small quantities of water or, in the case of alcohols higher than methanol, of aldehydes and ketones.

In compound (A), the bond between the $[Co(CO)_4]^-$ ion and the positively charged carbon atom of the carbonium ion is formed *via* the carbon atom of one of the CO groups[104]. It is possible that in this case, under the influence of electrophilic reagents, the $[Co(CO)_4]^-$ ion becomes asymmetric, with the production of higher reactivity in one of the CO groups relative to the three others. The formation of a bond to the central Co atom at the centre of the tetrahedron formed by the four CO groups is unlikely. A bond *via* the oxygen of a CO group is also unlikely, since as in the case of the CO molecule, the oxygen in carbonyls and carbonyl hydrides tends to retain a positive charge[126].



From this mechanism it can be seen that cobalt carbonyl hydride cannot be regenerated without the participation of a compound with labile hydrogen R'H, and that without this compound the reaction cannot take place. The reaction rate therefore depends on the reactivity of R'H. The greatest activity is shown by hydrogen itself, which may react in the presence of water, alcohols, etc. In our opinion, this feature does not quite fit into the proposed mechanism, since the hydrogen in the H_2 molecule can hardly be regarded as labile.

A very similar mechanism was proposed by Kirch and Orchin[127]:

$$2HCo(CO)_4 + RCH{=}CH_2 + CO \longrightarrow (HCo(CO)_4)_2 \cdot RCH{=}CH_2 \cdot CO \longrightarrow$$
$$\longrightarrow Co_2(CO)_8 + RCH_2CH_2CHO.$$

This was based on the observed formation of a stable $2HCo(CO)_4$.alkene.CO complex in the reaction of an alkene, CO, and carbonyl hydride at room temperature and atmospheric pressure. This complex begins to decompose even at 25°, with the liberation of CO and the formation of aldehyde.

Breslow and Heck[128] suggested that the reaction proceeds with the participation of cobalt carbonyl hydride according to the scheme:

$$RCH{=}CH_2 + HCo(CO)_4 \longrightarrow RCH_2CH_2Co(CO)_4 \longrightarrow RCH_2CH_2COCo(CO)_3 \xrightarrow{CO}$$
$$\xrightarrow{CO} RCH_2CH_2COCo(CO)_4 \xrightarrow{HCo(CO)_4} RCH_2CH_2CHO + Co_2(CO)_8.$$

This scheme is confirmed by the synthesis of compounds $RCo(CO)_4$, where R = CH_3, C_2H_5, $C_6H_5CH_2$, from $NaCo(CO)_4$ and RX; these compounds add on one CO molecule to form the intermediate compound of the last stage $CH_3CO{-}Co(CO)_4$, which reacts with cobalt carbonyl hydride to give the aldehyde and cobalt carbonyl:

$$CH_3COCo(CO)_4 + HCo(CO)_4 \longrightarrow CH_3CHO + Co_2(CO)_8.$$

This mechanism, however, does not agree with the fact that the reduction of $CH_3COCo(CO)_4$ with hydrogen at 25° and 200 atm stops completely at high CO pressure. The compound being reduced is probably $CH_3COCo(CO)_3$, and not $CH_3COCo(CO)_4$. The retarding action of CO can be attributed to the conversion of the acylcobalt tricarbonyl into the inactive acylcobalt tetracarbonyl. Thus a more probable scheme is

$$RCH{=}CH_2 + HCo(CO)_3 \longrightarrow RCH_2CH_2Co(CO)_3 \xrightarrow{CO} RCH_2CH_2COCo(CO)_3 \xrightarrow{H_2}$$
$$\xrightarrow{H_2} RCH_2CH_2COH + HCo(CO)_3.$$

The reactivity of alcohols decreases with increase in molecular weight[104]. When small quantities (1–10 mole %) of methanol are present in the butanol, the reaction products contain considerable quantities of methyl esters. In the case of butanol the reaction is initiated by the hydrogen liberated on dehydrogenation. Butyraldehyde is detected. In the case of methanol, no significant quantities of formaldehyde are produced, but dehydration to dimethyl ether takes place readily. Considerable quantities of methyl acetate are detected, probably formed according to the reaction

$$CH_3OCH_3 + CO \rightarrow CH_3COOCH_3.$$

The methyl acetate cannot be formed from acetic acid, since the latter is not obtained by direct synthesis from CO and methanol at temperatures below 250° and in the absence of halides or halogens.

For carboxylation reactions in the presence of metallic nickel and nickel halides on carriers, Bhattacharyya[129] proposed two basic schemes with intermediate metal carbonyl halide complexes or carbonium ions. The first scheme gives complexes of the type $M(CO)I_2$ (where M = Co, Fe, Ni), which subsequently react with other reagents; CO may be added on with the liberation of halogen. For example,

$$NiI_2 + CO \longrightarrow Ni(CO)I_2 \xrightarrow{3CO} Ni(CO)_4 + I_2,$$

$$NiCOI_2 + CH_3OH \longrightarrow CH_3COOH + NiI_2.$$

Here NiI_2 is regenerated.

In the reaction of Fe and Co halides under pressure, complexes of composition $Co(CO)I_2$, $Fe(CO)_2I_2$, $[Fe(CO)_3Br_2]_3$, etc. are formed[125,130,131]. $Co(CO)I_2$ is obtained[129] at 200 atm and 100° in the form of a dark red crystalline substance with a very high CO dissociation pressure even at room temperature. The analogous nickel complexes could not be isolated, although they may be formed as unstable intermediate products. The electronic configurations of Ni, Co, and Fe indicate that the stability of these complexes decreases in the order Fe > Co > Ni. This may explain the above order of decrease in activity, depending on the nature of the metal and halogen. On the one hand, the Ni complexes are the least stable and hence more reactive. On the other hand, iodide forms complexes more readily than bromide and chloride. The scheme involving intermediate carbonyl halide complexes cannot, however, explain the activating action of traces of water on the catalyst. The other scheme, based on the carbonium-ion theory, is therefore more probable, in view of the acidic character of the catalysts on silica gel.

It was mentioned above that the presence of traces of water is necessary to preserve the activity of the MX_2 catalysts. This is evidently required for the formation of HI according to the reaction

$$NiI_2 + H_2O \longrightarrow NiO + 2HI,$$

or, according to Reppe,

$$NiI_2 + 5CO + H_2O \longrightarrow Ni(CO)_4 + 2HI + CO_2.$$

Traces of nickel oxide are in fact detected in the spent catalyst. The function of the HI may be to displace the extremely active CO from the nickel carbonyl with regeneration of NiI_2:

$$2HI + Ni(CO)_4 \longrightarrow NiI_2 + 4CO + H_2,$$

or to activate other components of the reaction

$$CH_3OH + HI \rightleftharpoons (CH_3HOH)^+ + I^- \rightleftharpoons \overset{+}{C}H_3 + H_2O + I.$$

The resulting carbonium ion reacts with CO:

$$\overset{+}{C}H_3 + :\overset{-}{C}:::\overset{+}{O}: \rightleftharpoons CH_3C:::\overset{+}{O} \rightleftharpoons CH_3{-}\overset{+}{C}::O:.$$

Water then reacts, with the formation of acetic acid:

$$CH_3\overset{+}{C}::O: + H_2O \longrightarrow \underset{\displaystyle OH}{CH_3C::O} + \overset{+}{H}.$$

The H^+ then attacks another alcohol molecule and the reaction continues. The mechanism of other reactions involving the formation of acids and esters may be represented in this way[110–118].

A mechanism for the carboxylation of alcohols with CO in the presence of an Ni catalyst has been proposed[43]:

$$R{-}CH_2OH + HI \longrightarrow R{-}CH_2I + H_2O,$$

$$R{-}CH_2I + CO + H_2O \xrightarrow[Ni(CO)_4]{} R{-}CH_2COOH + HI.$$

The HI necessary for this reaction is obtained in the formation of $Ni(CO)_4$ from NiI_2 and CO. The $Ni(CO)_2I_2$ acts as active CO carrier. One further reaction takes place:

$$Ni(CO)_4 + 2HI \longrightarrow NiI_2 + 4CO + H_2.$$

The reactions leading to the conversion of CO have been described earlier[43]. Carboxylic acids with the iso-structure are obtained in the carboxylation of higher alcohols as a result of isomerisation of the intermediate primary halogeno-derivative to secondary and tertiary derivatives.

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UNSATURATED ORGANOBORON COMPOUNDS

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I. INTRODUCTION

The chemistry of organoboron compounds is at present undergoing intensive development. A number of reviews [1-8] dealing with different aspects of this subject have appeared within a comparatively short time interval.

The present review deals with achievements in the field of unsaturated organoboron compounds and covers the literature up to 1962, together with some later papers. It does not deal with alkylboranes containing unsaturated groups; there are two representatives of this class of compound – allyldecaborane [9] and di(allylamino)borane [10]. These compounds are of interest because of a number of unique features in their structure, the possibility of using them as monomers for the production of heat-resistant polymers, and their use as intermediate products in the preparation of a wide variety of boron compounds. Alkenylboronic and dialkenylborinic acids, their esters, and trialkenylborons exhibit more effective insecticidal and fungicidal properties than the analogous boron compounds with saturated radicals. On condensation with polyisocyanates and polyisothiocyanates, alkenylboronic acids give boron-containing polyamides. Polymers based on *p*-vinylphenylboronic acid may be used as materials which are readily shaped and rolled, and the copolymer of this acid with styrene can be formed into threads. The thioesters of chlorovinylboronic acid can be used as plasticisers and also as monomers for the production of film- and fibre-forming materials. The use of octadec-9-enylboronic acid derivatives as additives to poly(vinyl chloride) to improve certain of its properties has been suggested.

B-Allylborazoles can be used as additives to rocket fuels, active ingredients in insecticides, bactericides, and herbicides, and as components of heat-resistant compositions, plasticisers, scintillation indicators, additives to polymers to give neutron-absorbing properties, etc.

II. TRIALKENYLBORONS AND THEIR COMPLEXES

The first alkenylborons – methyldivinylboron, dimethylvinylboron, trivinylboron, dimethylpropenylboron, and methyldipropenylboron – were prepared by the reaction of vinylsodium and propenyllithium with dimethylboron bromide at low temperature [11-13]. An improved method for the preparation of unsymmetrical alkenylmethylboron compounds involves the reaction of chlorodivinylboron or di-

chlorovinylboron with dimethylzinc[14]. Trivinylboron[15] can be obtained in 70% yield by the reaction of vinylmagnesium bromide with boron trifluoride in absolute ethyl ether with a threefold excess of magnesium. Trivinylboron and tripropenylboron were prepared in low yield by the reaction of vinylmagnesium chloride and propenylmagnesium chloride respectively with boron trichloride in tetrahydrofuran[16]. Tripropenylboron can also be obtained from propenylmagnesium chloride and the ether addition compound of boron trifluoride[17]. The same method has been used to prepare tributenylboron, tripentylboron, and trihexenylboron[18].

The first report of a synthesis of triallylboron[19] appeared in the patent literature in 1954. More detailed information on the preparation of triallylboron by the reaction of boron trifluoride or trichloride with allylmagnesium halides appeared in 1958[20,21]. A method has been proposed for the preparation of triallylboron[22] from allylaluminium bromide $(C_3H_5)_3Al_2Br_3$ and butyl borate or the ether addition compound of boron trifluoride.

Tri-2-methallylboron was prepared from the corresponding organomagnesium halide and boron halides or borate in ether at 20–60°.[23]

Tri-*p*-styrylboron[24] and tri-ω-styrylboron[25] were prepared by the reaction of *p*- and ω-styrylmagnesium bromide respectively with boron trifluoride.

Petrov *et al.*[26] reported the preparation of dibutyl(isopropenylethynyl)boron according to the scheme

$$(C_4H_9)_2BCl + BrMgC{\equiv}C{-}C(CH_3){=}CH_2 \xrightarrow{\text{ether}} (C_4H_9)_2BC{\equiv}C{-}C(CH_3){=}CH_2 + MgBrCl.$$

Some acetylenic compounds of boron were prepared from acetylenedimagnesium bromide and dialkylboron iodides[27,28]. Disproportionation of di-(2-chlorovinyl)boron chloride in the liquid phase at 140–190° in the absence of catalyst with the simultaneous distillation of the resulting 2-chlorovinylboron dichloride was used to prepare tri-(2-chlorovinyl)-boron[29,30].

Activated carbon inhibits the disproportionation of di-(2-chlorovinyl)boron chloride to tri-(2-chlorovinyl)boron. Di(chlorovinyl)ethylboron was prepared by the analogous thermal disproportionation of (2-chlorovinyl)ethylboron chloride[30].

An attempt to prepare (2-chlorovinyl)diethylboron by the vinylation of diethylboron chloride and disproportionation of di(chlorovinyl)ethylboron was unsuccessful[30,31]. In the vapour phase the reaction between boron trichloride and acetylene in the presence of typical vinylating catalysts gave, in addition to the halogeno-compounds, a small quantity of tri-(2-chlorovinyl)boron[32]. An attempt to prepare this compound by the reaction of acetylene with di-(2-chlorovinyl)boron chloride at 140–180° was unsuccessful[30].

Tri(perfluorovinyl)boron was prepared in good yield by the reaction of dimethyldi(perfluorovinyl)tin with di(perfluorovinyl)boron chloride in the ratio 1 : 2 at 50°.[33] It is suggested that trialkenylborons are formed as intermediate products in the hydroboration of acetylene derivatives, for example pent-2-yne and hex-2-yne[34]:

$$3R{-}C{\equiv}C{-}R + {}^1/_2(BH_3)_3 \xrightarrow{0^\circ} \begin{pmatrix} R{-}C{-}H \\ \| \\ R{-}C{-} \end{pmatrix}_3 B.$$

The treatment of alkynes with inner multiple bonds, such as hex-3-yne, with hydroborating agents gives the corresponding vinylboron compounds. Under the same conditions, α-alkynes, for example hex-1-yne, undergo chiefly dihydroboration[35]. The hydroboration of but-1-yne, pent-1-yne, and hex-1-yne by *t*-butylborine-trimethylamine proceeds vigorously according to the equation[36]

$$t\text{-}C_4H_9BH_2.N(CH_3)_3 + 2RC{\equiv}CH \rightarrow t\text{-}C_4H_9B(CH{=}CHR)_2 + N(CH_3)_3.$$

The reaction of sodium tetracyclohex-1-enylborate with lead naphthenate gives tricyclohex-1-enylboron and tetracyclohex-1-enyllead[37].

Sodium tetra(phenylethynyl)borate was prepared by the reaction of boron halides with an excess of phenylethynylsodium at -60°. The reaction apparently takes place in two stages; the initial product is $(C_6H_5C{\equiv}C)_3B$, which then adds on a molecule of phenylethynylsodium[38]. The magnesium salt $Mg[B(C{\equiv}C{-}C_6H_5)_4]_2$ was prepared by the reaction of phenylethynylmagnesium bromide and boron trifluoride

$$2BF_3 + 8C_6H_5C{\equiv}C{-}MgBr \rightarrow 3MgF_2 + 4MgBr_2 + Mg[B(C{\equiv}CC_6H_5)_4]_2.$$

The addition of NH_4^+ ions to an aqueous solution of this salt precipitates ammonium tetra(phenylethynyl)borate $NH_4[B(C{\equiv}CC_6H_5)_4]$ quantitatively[39]. Sazonova and Kronrod[40] prepared this compound by the reaction

$$KBF_4 + C_6H_5C{\equiv}CMgBr \rightarrow [KB(C{\equiv}CC_6H_5)_4] \xrightarrow{NH_4Cl} NH_4B(C{\equiv}CC_6H_5)_4.$$

Acidification of the above salts gives tri(phenylethynyl)-boron, which was separated in the form of molecular compounds with tetrahydrofuran, amines, and pyridine[41].

When the dimethylamine addition compound of diethyl ethylboronate was boiled with $C_4H_9C{\equiv}CNa$ for 1 h in ether, the product was the amine complex of ethyldi(hex-1-ynyl)-boron $C_2H_5(C_4H_9C{\equiv}C)_2B.NH(C_2H_5)_2$. In the same way $CH{\equiv}CNa$ and boron trifluoride in pyridine gave a dark red precipitate consisting of the complex compound $(HC{\equiv}C)_3B.NC_5H_5$. The ether addition compound of boron trifluoride under analogous conditions (or a solution of BF_3 in hydrocarbons) at -70° gave $Na[B(C{\equiv}CH)_4]$. Di(methylethynyl)-magnesium $(CH_3C{\equiv}C)_2Mg$ and $Cl_3B.NH(CH_3)_2$ in pyridine at 0° rapidly (15 min) gave $(CH_3C{\equiv}C)_3B.NH(CH_3)_2$.[42] Some complexes of tri(phenylethynyl)boron with Lewis bases were described by Ashby and Foster[43].

When triphenylboron and phenylethynyllithium were heated in ether and then cooled to -70°, the complex $Li[B(C_6H_5)_3(C{\equiv}CC_6H_5)]$ was formed[44]. The reaction of $F_3B.NC_5H_5$ with (phenylethynyl)magnesium bromide at different reagent ratios gives only $Mg[B(C{\equiv}CC_6H_5)_4]_2$.[45] The reaction of $(C_6H_5)_2BOCH_2CH_2NH_2$ with $RC{\equiv}CMgBr$ gave the compounds $(C_6H_5)(RC{\equiv}C)B.NC_5H_5$ (where R = H, CH_3, C_6H_5, *p*-BrC_6H_4, 9-methylanthryl, $(CH_3)_3Si$, $(CH_3)_3SiCH_2$, C_2H_5S, and $(C_6H_5)_2B.NC_5H_5$).[45]

Vinylboron compounds are of interest, since the π electrons of the vinyl group are close to a boron atom with an empty p_π orbital, so that a mesomeric effect is produced:

$$CH_2{=}CH{-}B\langle \longleftrightarrow {}^+CH_2{-}CH{=}\bar{B}\langle .$$

This effect has a considerable influence on the properties of alkenylborons. Thus the presence of the vinyl or propenyl group stabilises the corresponding unsymmetrical compounds. The degree of decomposition of dimethylvinylboron kept for 5 days at room temperature was 33%. The presence of a second vinyl group increases the stability of the compound. Thus methyldivinylboron remained almost unchanged after boiling for 1 h at 100° and only slight decomposition was observed when the compound was heated at 100° for 70 h. The increased stability of these compounds is due to the fact that the phenomenon of mesomerism in alkenylboranes facilitates the production of a

planar configuration in the compounds and hence inhibits their disproportionation[12].

Trivinylboron is monomeric in the gaseous state but in the liquid phase it changes from the monomeric to the dimeric form and compounds of high molecular weight[46]. When heated at 226° for 4 h, tri-(2-chlorovinyl)boron decomposes partly to acetylene, hydrogen chloride, and di-(2-chlorovinyl)boron chloride[30]. Tri(perfluorovinyl)-boron in the gaseous phase does not undergo appreciable decomposition after 7 days at room temperature, but when heated at 100° for 5 h it decomposes completely to perfluorovinylboron difluoride and boron trifluoride[33].

Diallyldiborane and tetraallyldiborane were obtained by boiling triallylboron in an atmosphere of nitrogen[47].

The decomposition temperatures of the complexes of amines with tri(phenylethynyl)boron lie between 210° and 220°.[41]

$$C_6H_5C{\equiv}CB\langle \cdot NH_3 \rightarrow C_6H_5C{\equiv}CH + \rangle B \cdot NH_3 .$$

Unlike saturated compounds of boron, trivinylboron is not oxidised in contact with dry air at 25°. The behaviour of methyldivinylboron towards oxidation is intermediate between that of trivinylboron and that of the readily-oxidised trialkylborons.

Tri-(2-chlorovinyl)boron and (2-chlorovinyl)diethylboron are oxidised rapidly in air with spontaneous ignition[30]. Similar behaviour is shown by triallylboron, tributenylboron, tripentylboron, and trihexenylboron[18,19]. Tri(perfluorovinyl)boron ignites in air and burns with a smoky flame[33]. Organoboron compounds with triple bonds are extremely readily oxidised[27,45,48]. Unsaturated organoboron compounds obtained by hydroboration of the corresponding unsaturated hydrocarbons readily undergo protolysis by glacial acetic acid at 0° to form the corresponding *cis*-olefins[34,35]:

$$\left(\begin{matrix} R-C-H \\ \| \\ R-C- \end{matrix}\right)_3 B + CH_3COOH \xrightarrow{0^\circ} 3 \begin{matrix} R-C-H \\ \| \\ R-C-H \end{matrix} + B(OCOCH_3)_3 .$$

Tri-(2-chlorovinyl)boron and (2-chlorovinyl)diethylboron are readily hydrolysed in air and acetylene is liberated on treatment with a 10% solution of alkali[30]. The reaction of water with tri(perfluorovinyl)boron at 120° for 15 h gives trifluoroethylene; this reaction does not take place at room temperature[33]. The corresponding dialkylborinic acids R_2BOH are formed by the hydrolysis of the compounds $R_2BC{=}CBR_2$.[27]

Vinyl derivatives of boron, and also tributenylboron, tripentenylboron, and trihexenylboron, are unaffected by water at room temperature[12,18]. The complexes of tri-(phenylethynyl)boron with amines are not decomposed by water; the compound $(C_6H_5C{\equiv}C)_3B.OC_4H_8$ is decomposed slowly by cold water and the reaction with water at 50° leads to complete decomposition:

$$(C_6H_5C{\equiv}C)_3B \cdot OC_4H_8 + 3H_2O \xrightarrow{50^\circ} B(OH)_3 + 3C_6H_5C{\equiv}CH + C_4H_8O .$$

The reaction of the complex of tri(phenylethynyl)boron with alcohols leads to the formation of phenylacetylene and trialkyl borate[41].

Treatment with ammoniacal silver hydroxide solution gives methane and hexa-2,4-diene from methyldipropenylboron, and ethylene and butadiene from trivinylboron[12]. Treatment of the complex $Li[B(C_6H_5)_3(C{\equiv}CC_6H_5)]$ with acids at -30° gives phenylacetylene, and the reaction with aqueous iodine solution gives phenylethynyl iodide[43].

Treatment of tributenylboron with a solution of bromine in carbon tetrachloride at a molar ratio of 1 : 3 apparently leads to the addition of bromine across the double bond. A slight excess of bromine is slowly decolorised with the liberation of HBr.[18] Triallylboron reacts readily with bromine at -35° with rupture of the B–C bond and the formation of 1,2,3-tribromopropane as chief product[22].

On hydrogenation under pressure over Raney nickel as catalyst at room temperature, triallylboron adds on 3 moles of hydrogen with the formation of tripropylboron[22]. Hydrogenation of $(C_6H_5)_2(RC{\equiv}C)B.NC_5H_5$ in the presence of platinum gives $(C_6H_5)_2(RCH_2CH_2)B.NC_5H_5$.[45]

Trivinylboron adds on $HSi(CH_3)_2OSi(CH_3)_3$ under the influence of hydrogen chloroplatinate(II) at 100°[48]:

$$3HSi(CH_3)_2OSi(CH_3)_3 + (CH_2{=}CH)_3B \rightarrow [(CH_3)_3SiOSi(CH_3)_2CH_2CH_2]_3B .$$

Mikhailov and Tutorskaya found that at -15° triallylboron reacts with an equimolar quantitiy of ethanethiol to give propene and ethyl di(allylthio)borinate. The action of 2 moles of ethanethiol gives diethyl allylthioborinate[49].

The reactions of triallylboron with carboxylic acids and alcohols have been studied in detail[20,21,50]. Thus the reaction with glacial acetic acid gives diallylboron acetate and the reactions with ethanol and allyl alcohol give diethyl and diallyl allylboronates respectively.

An alcoholic solution of ammonium tetra(phenylethynyl)-borate is decomposed almost quantitatively by ammoniacal copper(I) chloride solution with the formation of yellow copper phenylacetylide and by mercury(II) iodide with the formation of di(phenylethynyl)mercury[40].

III. ALKENYLBORONIC AND DIALKENYLBORINIC ACIDS AND THEIR ANHYDRIDES

The first representative of this class of compound — 2-chlorovinylboronic acid — was prepared by Arnold in 1946.[32] Later it was found that this acid is formed by the decomposition of 2-chlorovinylboron dichloride with water and is stable in air[52]. Di-(2-chlorovinyl)boronic acid was obtained as a colourless liquid by hydrolysing di-(2-chlorovinyl)boron chloride. This acid readily liberates acetylene when treated with aqueous alkali[52].

A number of alkenylboronic acids — vinylboronic, isopropenylboronic, and 1-methylvinylboronic — were prepared by Normant and Braun[17,53,54] according to the following general scheme

$$\rangle C{=}C-MgX + B(OCH_3)_3 \rightarrow \rangle C{=}C-B(OCH_3)_2 \xrightarrow{H_2O} \rangle C-C-B(OH)_2 .$$

The anhydrides of the above acids are formed by azeotropic dehydration or by heating *in vacuo*. The anhydrides add on water and alcohols to give the corresponding boronic acids and their esters. Ammoniacal $AgNO_3$ solution decomposes these acids slowly in the cold and rapidly with heating, to give the corresponding olefins and metallic silver. Hydrogen peroxide and other peroxides break the boron–carbon bond with conversion of the original compounds to the corresponding aldehydes and ketones[54]:

$$\rangle C{=}C-B\langle \xrightarrow{H_2O_2} \rangle C{=}C-OH \rightarrow \rangle CH-C{=}O .$$

Isobutenylboronic acid was prepared in 7% yield by the reaction of isobutenyllithium with trimethyl borate with subsequent hydrolysis of the reaction product[55]. Hydrolysis of n-butyl vinylboronate and n-butyl 1-methylvinylboronate gave the corresponding acids[56].

The action of chlorine on n-butylboronic anhydride gave n-butenylboronic anhydride and hydrogen chloride. Treatment of this anhydride with aluminium chloride gave two products, unstable at room temperature, which were not identified[57].

Allylboronic acid was isolated as its anhydride by the reaction of triallylboron with water:

$$(C_3H_5)_3B + 2H_2O \rightarrow \underset{\downarrow}{[C_3H_5B(OH)_2]} + 2C_3H_6.$$
$$(C_3H_5BO)_3$$

The first stage of the reaction apparently involves the formation of diallylborinic acid, which undergoes further hydrolytic splitting at the boron–carbon bond[21]. The preparation of diallylborinic anhydride by the hydrolysis of methyl diallylborinate was also reported by Rothstein and Saville[58]. This anhydride decomposes slowly in air to boric acid. Allylboronic acid was prepared by Roigh and Erikson[59].

A much more stable product is styrylboronic acid, which can be kept unchanged for a prolonged period. It is prepared from styrylmagnesium bromide and potassium fluoroborate with subsequent hydrolysis and oxidation of the resulting complex salt[37]:

$$C_6H_5CH{=}CHMgBr + KBF_4 \rightarrow [KB(CH{=}CHC_6H_5)_4] \xrightarrow[O_2]{H_2O} C_6H_5CH{=}CHB(OH)_2.$$

Mel'nikov and Rokitskaya[60] prepared this acid from styrylmagnesium bromide and isobutyl borate. When dried, the acid is partly converted to the anhydride. The addition of an ethereal solution of $FeCl_3$ to an ethereal solution of styrylboronic acid leads to rapid formation of the anhydride. Cryoscopic measurements in benzene show that this exists as the dimer. The chemical properties of styrylboronic acid are analogous to those of arylboronic acids. When heated with mercury(II) chloride it readily forms styrylmercury chloride:

$$C_6H_5CH{=}CHB(OH)_2 \xrightarrow{HgCl_2} C_6H_5CH{=}CHHgCl.$$

The action of thallium trichloride gives distyrylthallium chloride[40]:

$$2C_6H_5CH{=}CHB(OH)_2 \xrightarrow{TlCl_3} (C_6H_5CH{=}CH)_2TlCl.$$

The preparation of *p*-vinylphenylboronic acid from *p*-vinylphenylmagnesium bromide and trimethyl borate at -70° with subsequent hydrolysis of the reaction product has been proposed[53,61,62]. The highest yield of acid was obtained by Normant and Braun[53] (80%) and Cazes[61] (75%) using pure reagents. Letsinger and Hamilton[63] used this method to prepare *p*-vinylphenylboronic and *p*-isopropenylphenylboronic acids. They used tributyl borate as starting material. These acids react with *o*-phenylenediamine to form dihydrobenzoboradiazole derivatives[61]. A new method for the preparation of *p*-vinylphenylboronic acid was proposed by Hoffmann and Thomas[64-66]; the acid was prepared by brominating *p*-ethylphenylboronic anhydride with subsequent removal of hydrogen bromide:

$$(CH_3{-}\underset{\underset{Br}{|}}{CH}{-}C_6H_4BO)_3 \xrightarrow{-HBr} (CH_2{=}CHC_6H_4BO)_3 \xrightarrow{H_2O} CH_2{=}CHC_6H_4B(OH)_2.$$

p-Ethylphenylboronic acid was prepared by the reduction of *p*-vinylphenylboronic acid with hydrogen on a platinum catalyst[62].

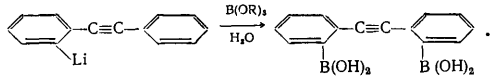
A convenient method for the dehydration of the acid to the anhydride is by drying *in vacuo* over phosphorus pentoxide[60]. When *p*-vinylphenylboronic acid was heated at 100° in a solvent (benzene, xylene, or carbon tetrachloride) until the liberation of water stopped, the anhydride was obtained in yields of more than 95%.[67,68]

Di-(*p*-vinylphenyl)boronic acid $(CH_2{=}CHC_6H_4)_2BOH$ was prepared by the reaction of 2 moles of *p*-vinylphenylmagnesium chloride with butyl borate, followed by hydrolysis; the acid was isolated as the aminoethyl ester in 38% yield[63].

Attempts to prepare *p*-vinylphenylboronic acid from *p*-vinylphenyllithium and tributyl borate were unsuccessful. *p*-Isopropenylphenylboronic acid was prepared from *p*-isopropenylphenyllithium and butyl borate[63].

Two methods for the preparation of *o*-vinylphenylboronic acid have been proposed: the reaction of *o*-vinylphenylmagnesium chloride with tributyl borate, followed by hydrolysis, and the dehydrobromination of 2-(1-bromoethyl)phenylboronic anhydride with quinoline at 130–135°.[65,66,69] *m*-Vinylphenylboronic acid was prepared in analogous fashion[66]. On condensation with nitromethane and acetone, *p*-formylphenylboronic acid formed *p*-(β-nitrovinyl)phenylboronic and *p*-(β-acetylvinyl)phenyl boronic acids respectively[70].

Letsinger and Nazy[71] described a new type of diboronic acid — 2,2′-tolandiboronic acid — obtained in 86% yield by the reaction of the corresponding lithium derivatives with tributyl borate and water:



In alkaline media this acid readily forms heterocyclic compounds; the reaction with *o*-phenylenediamine gives bis(dihydrobenzo)boradiazole and the reaction with hydrogen peroxide gives 2-(*o*-hydroxyphenyl)benzofuran. The action of water at 200° lead to the formation of deoxybenzoin.

2-Tolanboronic acid is analogous to 2,2′-tolandiboronic acid, but it is not isomerised in alkaline media and is oxidised by hydrogen peroxide to hydroxytolan. This acid, and also 2,2′-stilbenediboronic acid, were prepared from the corresponding lithium derivatives and tributyl borate, with subsequent hydrolysis of the reaction mixture[67]. Compounds with hydrophilic groups, intended for use in cancer therapy, include the acid $HOOCCH{=}CHCONHC_6H_4B.(OH)_2$, prepared by acylating aminophenylboronic acid with maleic anhydride[72]. The double bond in this acid is hydrogenated in the presence of PtO_2.

Maitlis[73,74] reported the preparation of *o*-(4-phenylbuta-1,3-dienyl)phenylboronic anhydride from *o*-bromophenyl-4-phenylbuta-1,3-diene, butyllithium, and butyl metaborate. This anhydride has the *trans,trans*-configuration.

IV. ESTERS OF ALKENYLBORONIC AND DIALKENYLBORINIC ACIDS

The methods for preparing esters of unsaturated acids involve the alcoholysis of various organoboron compounds.

a. Alcoholysis of halogeno-compounds of boron. Lazier and Salzberg[75] used the reaction of methanol, with chlorovinylboron dichloride to prepare a number of esters of unsaturated acids, for example dimethyl chlorovinylboronate:

$$ClCH{=}CHBCl_2 + CH_3OH \rightarrow ClCH{=}CHB(OCH_3)_2.$$

A cyclic ester of this acid, $ClCH{=}CHBOCH_2{-}CH_2$ (O), was prepared from chlorovinylboronic acid and ethylene glycol. In analogous fashion, ethanolysis of di(chlorovinyl)boron chloride gave ethyl di(chlorovinyl)borinate[52]:

$$(ClCH{=}CH)_2BCl + C_2H_5OH \rightarrow (ClCH{=}CH)_2BOC_2H_5 + HCl.$$

b. Alcoholysis of alkenylboronic acids and their anhydrides. Several esters of vinylboronic and propenylboronic acids are known. These were synthesised by the action of alcohol on benzene solutions of the corresponding acids[53]. Later the yield of n-butyl propenylboronate was increased to 95% by using the anhydride of the acid[17].

Di-n-butyl and di-n-hexyl isopropenylboronates and the cyclic ester

$$(CH_3)_2C{=}CHBOCH_2CH_2 \quad (O)$$

are known[17,53]. This method has been used to prepare several esters of n-propenylboronic acid[17,53].

When *p*-vinylphenylboronic acid is heated in toluene solution with diethanolamine, the product is aminodiethyl *p*-vinylphenylboronate. The analogous reaction with butanol gave di-n-butyl *p*-vinylphenylboronate and that with allyl alcohol gave diallyl *p*-vinylphenylboronate[61,66]. With ethyl tartrate, *p*-vinylphenylboronic acid forms the corresponding ester[63].

An ester of a saturated organoboronic acid with unsaturated ester groups has also been prepared. The addition of an excess of allyl alcohol to di-n-butylborinic anhydride and removal of water gave allyl di-n-butyl borinate[76].

c. Hydrolysis and subsequent esterification of the products of the reaction of a borate with an alkenylmagnesium halide. This method is essentially a variation of the second method, since hydrolysis of the reaction products gives the corresponding acid. The borates used included trimethyl borate, triethyl borate, tributyl borate, and esters of metaboric acid:

$$RMgCl + B(OR')_3 \xrightarrow{HCl+H_2O} RB(OH)_2 \xrightarrow{R'OH} RB(OR')_2.$$

Mikhailov and Tutorskaya[77] prepared n-butyl vinylboronate by the action of vinylmagnesium bromide on trimethyl borate with subsequent hydrolysis and esterification of the reaction products. This ester was obtained by a similar method, but in lower yields, by Normant[17].

Diallyl allylboronate[20,21], dibutyl ethynylboronate, dibutyl butylethynylboronate[78], and 2-aminoethyl di-(*p*-vinylphenyl)borinate[63] were prepared in analogous fashion. An ester of metaboric acid can be used instead of the borate. Di-n-butyl allylboronate was prepared from allylmagnesium bromide and an ester of metaboric acid with subsequent decomposition of the reaction products with water and esterification with n-butanol[21]. Methyl and ethyl diallylborinates were prepared by Rothstein and Saville[58].

A much simpler method for the preparation of these esters is by the direct reaction of an alkenylmagnesium halide with borates. Thus the reaction of 1 mole of propenylmagnesium chloride with triethyl borate at -30° in tetrahydrofuran gives diethyl propenylboronate. When the latter is treated with a further mole of $CH_3CH{=}CHMgCl$, the product is ethyl dipropenylborinate[16]. Methyl allylboronate has been synthesised in low yield (6.8%) from allylmagnesium bromide and trimethyl borate[21].

Esters can also be prepared by the alcoholysis of the products of the reaction of borates with alkenylmagnesium halides. At a $(CH_3O)_3B : CH_3CH{=}CHMgBr$ ratio of 1 : 2, treatment of the reaction mixture with n-butanol gave n-butyl dipropenylborinate[17].

Zavgorodnii and Petrov[79] prepared esters of methylethynyl- and vinylethynyl boronic acids by hydrolysing the products of the reaction of methylethynyl- and vinylethynyl-magnesium bromide with tributyl borate at -40°.

d. The reaction of trialkenylborons, trialkenyl borates and esters with alcohols. The action of 1 and 2 moles of methanol on triallylboron at room temperature gives dimethyl allylboronate[21]. The dibutyl ester of this acid was obtained by the action of 2 moles of the alcohol on triallylboron[21,23], and the action of 1 mole of the alcohol gave butyl diallylborinate[21]:

$$(C_3H_5)_3B + C_4H_9OH \rightarrow (C_3H_5)_2B(OC_4H_9) + C_3H_6;$$

$$(C_3H_5)_3B + 2C_4H_9OH \rightarrow C_3H_5B(OC_4H_9)_2 + 2C_3H_6.$$

When 2-aminoethyl di-(*p*-vinylphenyl)borinate was mixed with 1-aminopropan-2-ol, the product was 2-amino-1-methylethyl di-(*p*-vinylphenyl)borinate[63].

e. Other methods. A method for preparing dipentyl allylboronate by the reaction in an autoclave between sodium, a borate, lithium chloride, and allyl bromide with subsequent hydrolysis of the reaction products and esterification with pentanol has been patented[81]. Meerwein and coworkers[82] prepared 2,2-dibromovinyl diethylborinate by the reaction of bromal with triethylboron:

$$B(C_2H_5)_3 + CBr_3CHO \rightarrow (C_2H_5)_2BOCH{=}CBr_2 \xrightarrow{CBr_3CHO} C_2H_5B(OCH_2{=}CBr_2)_2 +$$

$$+ C_2H_5B\begin{matrix}OCH{=}CBr_2\\OCH_2CBr_3\end{matrix}.$$

Allyl and methallyl diethylborinates were prepared by Rothstein and Saville[58] from diethylzinc and the corresponding borates:

$$Zn(C_2H_5)_2 + B(OR)_3 \rightarrow (C_2H_5)_2BOR + Zn(OR)_2.$$

Johnson *et al.*[83] isolated a small quantity of dibutenyl n-butylborinate as a by-product of the reaction of tributyl borate with t-C_4H_9OCl at -80°.

The esters of alkenylboronic acids are readily hydrolysed by water and this forms the basis of a method for preparing the acids. The action of aqueous solutions of bases or sodium bicarbonate also leads to very rapid hydrolysis in the case of dibutyl ethynylboronate, the ethynyl group being removed as acetylene[78]. On hydrogenation over $Pd/CaCO_3$ dibutyl vinylethynylboronate adds on 2 moles of hydrogen with the formation of dibutyl butenylboronate[79].

In the bromination of dibutyl vinylethynylboronate the first bromine molecule adds chiefly across the double bond[79]. Mikhailov and Aronovich[84] carried out the addition of bromine in the cold to di-n-butyl vinylboronate and allylboronate with the formation of di-n-butyl $\alpha\beta$-dibromoethylboronate and $\beta\gamma$-dibromopropylboronate respectively:

$$CH_2{=}CHB(OC_4H_9)_2 + Br_2 \rightarrow CH_2BrCHBrB(OC_4H_9)_2,$$

$$CH_2{=}CHCH_2B(OC_4H_9)_2 + Br_2 \rightarrow CH_2BrCHBrCH_2B(OC_4H_9)_2.$$

The resulting esters readily undergo β-breakdown under the influence of nucleophilic reagents. The addition of bromine to dibutyl ethynylboronate requires initiation: $BrCH{=}CBrB(OC_4H_9)_2$ is formed in 88% yield. Phosphorus pentachloride readily removes one butoxy-group from dibutyl vinylboronate[77]:

$$CH_2{=}CHB(OC_4H_9)_2 + PCl_5 \rightarrow CH_2{=}CHB(Cl)OC_4H_9 + C_4H_9Cl + POCl_3.$$

In the presence of azobisisobutyronitrile, dibutyl vinylboronate and isopropenylboronate add on CCl_4 with the formation of $CCl_3CH_2CHClB(OC_4H_9)_2$ and $CCl_3CH_2CCl(CH_3).B(OC_4H_9)_2$ respectively. The formation of 1 : 1 adducts of the above esters takes place much more readily with bromotrichloromethane in the presence of traces of initiator at 80°.[56,85]

Experiments were also carried out on the addition of chloroform and aldehydes to this ester; the former gave a telomer and the latter did not react. Matteson[85] suggests that dibutyl vinylboronate (I) reacts with free radicals ($X^{\cdot}$) to give intermediate radicals (II) which are stabilised by the boron–carbon π bond and subsequently react to give esters (III) containing different functional groups:

$$\underset{(I)}{CH_2{=}CHB(OC_4H_9)_2} \xrightarrow{X^{\cdot}} \underset{(II)}{XCH_2CH\text{------}B(OC_4H_9)_2} \xrightarrow{XY} \underset{(III)}{XCH_2CHYB(OC_4H_9)_2};$$

(III) a: X=CCl_3, Y=Cl;

b: X=CCl_3, Y=Br;

c: X=$HC_6H_{13}S$, Y=H.

In the presence of azobisisobutyronitrile, dibutyl ethynylboronate adds on bromotrichloromethane and hexanethiol to give $CCl_3CH{=}CBrB(OC_4H_9)_2$ and $C_6H_{13}SCH{=}CHB.(OC_4H_9)_2$ respectively. The light-catalysed addition of hexanethiol to dibutyl vinylboronate takes place rapidly even at -70°.[78]

Lazier and Salzberg[75] observed exchange of ester groups when dimethyl chlorovinylboronate was heated to 100° with octanethiol and dodecanethiol:

$$ClCH{=}CHB(OCH_3)_2 + 2C_{12}H_{25}SH \rightarrow ClCH{=}CHB(SC_{12}H_{25})_2 + 2CH_3OH.$$

Silanes are added on to diisobutyl vinylboronate and allylboronate in the presence of hydrogen chloroplatinate(II). The addition of trichlorosilane and methyldichlorosilane to the esters of unsaturated acids takes place under milder conditions than the addition to olefins, due to the activating influence of the boron atom on the double bond. No addition takes place in the absence of catalyst[86]:

$$CH_2{=}CHB(OC_4H_9)_2 + HSiCl_3 \rightarrow Cl_3SiCH_2CH_2B(OC_4H_9)_2;$$

$$CH_2{=}CHB(OC_4H_9)_2 + CH_3SiHCl_2 \rightarrow Cl_2(CH_3)SiCH_2CH_2B(OC_4H_9)_2;$$

$$CH_2{=}CH{-}CH_2B(OC_4H_9)_2 + CH_3SiHCl_2 \rightarrow Cl_2(CH_3)SiCH_2CH_2CH_2B(OC_4H_9)_2.$$

An attempt to replace the butoxy-groups in dibutyl vinylethynylboronate by ethyl groups by the reaction with ethyllithium at -70° gave dibutyl ethylboronate and vinylacetylene[79]:

$$CH_2{=}CH{-}C{\equiv}CB(OC_4H_9)_2 \xrightarrow{C_2H_5Li} [CH_2{=}CH{-}C{\equiv}C{-}B(OC_4H_9)_2(C_2H_5)]Li \rightarrow$$

$$\xrightarrow{HCl} [CH_2{=}CH{-}C{\equiv}CB(OC_4H_9)_2(C_2H_5)]H \rightarrow CH_2{=}CH{-}C{\equiv}CH + C_2H_5B(OC_4H_9)_2.$$

Dibutyl vinylboronate is an active dienophilic reagent and forms an adduct with cyclopentadiene. The ethynylboronate, although a less active dienophilic reagents, also forms an adduct with cyclopentadiene — dibutyl bicyclo-[2,2,1]hepta-2,5-dienylboronate[74].

V. ALKENYL ORTHOBORATES

Alkenyl orthoborates are prepared chiefly by the methods used for alkyl borates[1,2,5]: esterification of boric acid and esterification of alkylboron halides. Esterification of boric acid was used to prepare triallyl borate[87-91], tri-1-methallyl borate[92], tri-2-methallyl borate[93], and tri-3-methallyl borate[92]. Triallyl borate[94-97] was prepared by the esterification of boron trichlorode. A high yield (85%) is achieved by using n-pentane or methylene dichloride as solvents[98,99]. Tri-2-methallyl borate, tripropynyl borate[98], and tributenyl borate[92] were prepared in analogous fashion. Tri-1-methallyl borate can be obtained in 58% yield by the rapid removal of the resulting hydrogen chloride from the reaction sphere[92].

The reaction of phenyl allyl ether with BCl_3 at -80° gives tri-*o*-allylphenyl borate. It is suggested that the first stage in this reaction involves the Claisen rearrangement of the phenyl allyl ether to *o*-allylphenol, catalysed by Lewis acids[100].

Triallyl borate can be prepared from boron acetate and allyl alcohol in 50% yield[90]. Sodium borohydride reacts with allyl alcohol at room temperature in the presence of one equivalent of acetic acid[101]:

$$3C_3H_5OH + NaBH_4 + CH_3COOH \rightarrow (C_3H_5O)_3B + NaOCOCH_3 + 4H_2.$$

The triallyl borate obtained in these experiments has an unusually high refractive index (n_D^{20} = 1.4496).

Thomas proposed a method for the preparation of tri-2-methallyl borate from boric oxide, methallyl alcohol, toluene, and anhydrous copper sulphate with heating up to 110°.[102,103] The transesterification of triallyl borate with 2,6-di-t-butyl-4-methylphenol gave the mixed orthoborate $4\text{-}CH_3\text{-}2,6\text{-}(t\text{-}C_4H_9)_2C_6H_2OB(OCH_2CH{=}CH_2)_2$.[80]

Organoboron and organophosphorus halides have been used to prepare the following borates: diallyl 1-(dimethoxyphosphinyl)-2-trichloroethyl borate, diallyl 1-(ethoxyphenylphosphinyl)propyl borate, and diallyl 1-(diphenylphosphinyl)propyl borate[104]. 2,6-Diallylphenyl borate[105] and octadec-9-enyl borate[106] are also known.

The properties of triallyl borate have been studied in most detail[107,108]. The viscosity of triallyl borate, measured in a Cannon-Fenske-Ostwald viscometer, is 1.25 cS at 7°, 0.902 cS at 23.2°, and 0.747 cS at 37.8°.[80-90] The infrared spectra of triallyl borate were discussed in detail in a review by Washburn *et al.*[80] Alkenyl borates are readily hydrolysed[90,93]. Tri-*o*-allylphenyl borate is hydrolysed by water to *o*-allylphenol[100]. The mixed diallyl $2,6\text{-di-t-butyl-4-methylphenyl borate } 4\text{-}CH_3\text{-}2,6\text{-}(t\text{-}C_4H_9)_2.C_6H_2OB(OC_3H_5)_2$ is stable to hydrolysis[80].

Transesterification of tri-1-methallyl borate with octan-1-ol gives 1-methallyl alcohol and trioctyl borate; analogous treatment of tri-3-methallyl borate gives butenyl alcohol and trioctyl borate[92]:

$$B(OR)_3 + 3C_8H_{17}OH \rightarrow B(OC_8H_{17})_3 + 3ROH.$$

When treated with air at 125°, triallyl borate is converted to poly(triallyl borate)[87]. Triallyl borate reacts with HBr and HI to form both dealkylation and addition products[98]:

$$(CH_2{=}CH{-}CH_2O)_3B + 3HHal \begin{cases} \nearrow 3CH_2{=}CHCH_2Hal + B(OH)_3 \\ \searrow (HalCH_2CH_2CH_2O)_3B. \end{cases}$$

The addition of HHal takes place contrary to Markovnikov's rule. Gerrard *et al.*[98] observed no reaction between

triallyl borate and HCl at 20°. Gaseous HCl does not react at 120° with tri-1-methallyl borate and tri-3-methallyl borate. When these are heated for 4 h at 110° the products are butenyl chloride and boric acid[92]:

$$B(OR)_3 + 3HCl \rightarrow 3RCl + B(OH)_3.$$

The action of a concentrated solution of bromine in carbon tetrachloride on triallyl borate gives tri-(2,3-dibromopropyl)borate[96].

The reaction of boron trichloride with borates in the proportions indicated in the equations gave alkenyloxyboron chlorides only in the case of the but-3-enyl group:

$$2B(OR)_3 + BCl_3 \rightarrow 3BCl(OR)_2;$$

$$B(OR)_3 + 2BCl_3 \rightarrow 3BCl_2OR.$$

In the case of methallyl borates the reaction does not stop at this stage[92]:

$$3BCl(OR)_2 \rightarrow 3RCl + B_2O_3 + B(OR)_3;$$

$$3BCl_2OR \rightarrow 3RCl + B_2O_3 + BCl_3.$$

The intermediate compound di-1-methallyloxyboron chloride could be isolated only as the complex $[H_2C{=}CH{-}CH(CH_3)O]_2BCl.C_5H_5N$.[92]

Aldehydes and ketones are reduced to alcohols more effectively by triallyl borate than by triisopropyl borate[89,109]. Triallyl borate reacts with diethylzinc to form allyl diethylborinate[97]:

$$B(OC_3H_5)_3 + Zn(C_2H_5)_2 \rightarrow C_3H_5OB(C_2H_5)_2.$$

This method can also be used to prepare methallyl esters.

Orthoborates can be used as alkylating agents in Friedel–Crafts alkylations. Alkylation of benzene and toluene with triallyl borate in the presence of aluminium chloride gave 1,2-diphenylpropane[110] and 1,2-ditolylpropane[91] respectively. Replacement of aluminium chloride by ferric chloride in the alkylation of benzene by triallyl borate gives allylbenzene[111].

VI. ALKENYLBORON HALIDES

Borisov[52] proposed two convenient methods for preparing 2-chlorovinyl derivatives of boron: (1) double decomposition of organoantimony compounds with boron trichloride, and (2) the reaction of 2-chlorovinylmercury chloride or di-(2-chlorovinyl)mercury with boron trichloride.

Di-(2-chlorovinyl)boron chloride was prepared by Clark *et al.*[112] by the disproportionation of 2-chlorovinylboron dichloride when heated in the liquid phase at 100–125° in the presence of activated carbon with simultaneous distillation of the resulting boron trichloride:

$$2ClCH{=}CHBCl_2 \rightarrow (ClCH{=}CH)_2BCl + BCl_3.$$

The asymmetric stable chlorovinylethylboron chloride, which is not decomposed under vacuum-distillation conditions, can be prepared by the reaction of ethylboron dichloride with tri-(2-chlorovinyl)boron or by the reaction of ethylboron dichloride with acetylene. Activated carbon was used as catalyst in the second case[31]. Chloromethylvinylboron is formed when a mixture of BCl_3 and methyldivinylboron is kept for 1 h at 25°.[14]

Brinckmann and Stone[113] prepared divinylboron chloride by heating tetravinyltin with boron trichloride. An attempt to prepare divinylboron fluoride by the reaction of tetravinyltin with boron trifluoride or vinylboron difluoride was unsuccessful. This compound can be obtained in good yield by the reaction

$$(CH_2{=}CH)_2BCl \xrightarrow{SbF_3} (CH_2{=}CH)_2BF,$$

carried out at -80° for 35 h.[113] The perfluorovinyl compounds of boron are the first covalent organoboron compounds containing no hydrogen. One such compound — di(perfluorovinyl)boron chloride — was prepared from dimethyldi(perfluorovinyl)tin and boron trifluoride[33]:

$$(CF_2{=}CF)_2Sn(CH_3)_2 + BCl_3 \rightarrow (CF_2{=}CF)_2BCl + Sn(CH_3)_2Cl_2.$$

2-Chlorovinylboron dichloride was prepared by the reaction between boron trichloride and acetylene at 150–300° over a granulated catalyst consisting of $HgCl_2$ deposited on activated carbon[32]:

$$BCl_3 + C_2H_2 \xrightarrow{HgCl_2} ClCH{=}CHBCl_2.$$

This compound was obtained in good yield by Borisov *via* the corresponding organoantimony compound[52]:

$$(ClCH{=}CH)_3Sb + 3BCl_3 \rightarrow 3ClCH{=}CHBCl_2 + SbCl_3.$$

Equivalent quantities of 2-chlorovinylmercury chloride and boron trichloride in kerosene or benzene react as follows[52]:

$$ClCH{=}CHHgCl + BCl_3 \rightarrow ClCH{=}CHBCl_2 + HgCl_2.$$

Vinylboron dichloride was prepared by the reaction of divinylzinc or divinylmercury with boron trichloride. Vinylboron dibromide was prepared in analogous fashion[114]. A method was proposed for the preparation of vinylboron dichloride by the reaction of vinylmagnesium chloride with boron trichloride or an alkyl borate at 0–12°.[16] The same compound was prepared from tetravinyltin and boron trichloride. In the reaction of boron trichloride with alkylvinyltin compounds BCl_3 first adds to the vinyl group, so that compounds such as di-n-butyldivinyltin can be used for the preparation of vinylboron dichloride[113,115].

Organotin compounds can also be used to prepare vinylboron difluoride (yield 52%)[113]. The replacement of the tin compounds in this reaction by divinylmercury of divinylzinc[116,117] decreases the yield of vinylboron difluoride to 30% and 27% respectively. Perfluorovinylboron dichloride was prepared by the reaction of dimethyldi(perfluorovinyl)tin with boron trichloride. Perfluorovinylboron difluoride was prepared in analogous fashion from boron trifluoride, but in lower yield (18%). The best yield (57%) was achieved by the reaction of perfluorovinylboron dichloride with antimony trifluoride[33]:

$$CF_2{=}CFBCl_2 \xrightarrow{SbF_3} CF_2{=}CFBF_2.$$

Allylboron difluoride was prepared by heating boron trifluoride with tetraallyltin[113].

2-Chlorovinyl derivatives of boron fume slightly in air and become dark[52], and the perfluorovinyl compounds ignite (sometimes with detonation)[32].

Different vinylboron halides have different thermal stabilities. Thus vinylboron difluoride can be kept for several months without decomposition and no appreciable decomposition is observed even after heating at 200° for 20 h. Vinylboron dichloride undergoes slight decomposition when distilled at 80–100°. When stored for several months, vinylboron dichloride forms a small quantity of

an apparently polymeric white residue. The degree of decomposition of divinylboron chloride at room temperature after 24 h is not more than 3%, but divinylboron fluoride decomposes appreciably at room temperature after 24 h to form vinylboron difluoride and trivinylboron[113]. The thermal stability of vinylboron halides increases in the order

$$(CH_2=CH)_2BF < (CH_2=CH)_2BCl < CH_2=CHBCl_2 < CH_2=CHBF_2.$$

Allylboron difluoride is much less stable than vinylboron difluoride: the formation of BF_3 is observed after several minutes in the liquid phase at 0°.[113]

Perfluorovinylboron difluoride decomposes in the gaseous phase at room temperature at the rate of 5% per week. Perfluorovinylboron dichloride does not decompose after 5 h at 100° but BCl_3 is liberated when the compound is kept for several days at room temperature.

Di(perfluorovinyl)boron chloride decomposes completely to perfluorovinylboron dichloride and tri(perfluorovinyl)boron in one day at room temperature[32].

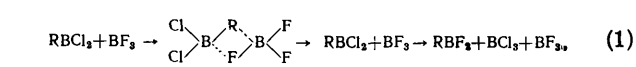
Ethylene is liberated when vinylboron difluoride comes into contact with water at 120°. Under identical conditions vinylboron dichloride and divinylboron chloride give ethylene in 85% and 30% yield respectively. The hydrolysis of vinylboron difluoride at room temperature, however, proceeds without removal of vinyl groups[113]. On treatment with water at room temperature perfluorovinylboron difluoride rapidly loses trifluoroethylene[33]. The sensitivity of various substituted boron halides towards removal of the vinyl groups with water increases in the order

$$C_2H_5BF_2 < (CH_2=CH)_2BCl < CH_2=CHBCl_2 < CH_2=CHBF_2 < CF_2=CFBF_2.$$

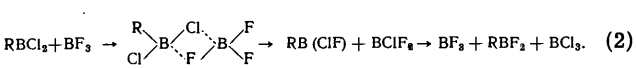
Perfluorovinylboron dichloride and di(perfluorovinyl)-boron chloride react with water at low temperatures forming chiefly perfluorovinylboronic acids[33]. 2-Chlorovinyl derivatives of boron split off acetylene when treated with 10% alkali[52]. Vinylboron halides are reduced by ammoniacal silver hydroxide solution at 100°. In the case of divinylboron halides (but not at room temperature) butadiene is formed in addition to ethylene[11,12]. Allylboron difluoride loses only propene[113]. Vinylboron difluoride reacts with boron trichloride according to the equation[113]

$$3CH_2=CHBF_2+2BCl_3 \rightleftarrows 2BF_3+3CH_2=CHBCl_2.$$

Two possible mechanisms for the reactions between boron trifluoride and vinylboron dihalides have been proposed:



(1)



(2)

The use of labelled boron (^{10}B) in BF_3 shows that no exchange of organic groups takes place in these reactions, so that the second mechanism is more probable[46].

A complex of vinylboron difluoride with trimethylamine has been prepared. The influence of the vinyl group attached to the boron atom on the acidity of these compounds has been compared with the influence of the corresponding saturated groups[118]. Vinylboron difluoride reacts with diethylzinc and trimethylaluminium. The chief product of the reaction with diethylzinc at room temperature is triethylboron and unreacted vinylboron difluoride. Trimethylaluminium reacts with liberation of heat and the formation of trimethylboron in 70% yield[113]. Di-(2-chlorovinyl)boron chloride reacts with thallium trichloride:

$$(ClCH=CH)_2BCl+TlCl_3 \xrightarrow{H_2O} (ClCH=CH)_2TlCl+B(OH)_3.$$

VII. BORON–NITROGEN COMPOUNDS CONTAINING ALKENYL GROUPS

Di-(2-chlorovinyl)boron chloride reacts with piperidine in cooled dry ether to give di-(2-chlorovinyl)boron-piperidine:

$$(ClCH=CH)_2BCl+2C_5H_{11}N \rightarrow (ClCH=CH)_2B \cdot NC_5H_{10}+C_5H_{11}N \cdot HCl.$$

This compound darkens in air and becomes viscous[52]. At room temperature triallylboron reacts readily with n-butylamine; with equimolar quantities of the reagents, diallyl-(n-butylamino)boron is formed[21]. The reaction with aniline takes place equally readily[119]. The first stage of the reaction of triallylboron with ethylamine, diethylamine, and ammonia gives complexes which lose propene when heated[119]:

$$(C_3H_5)_3B + (C_2H_5)_2NH \rightarrow (C_3H_5)_3B \cdot NH(C_2H_5)_2 \xrightarrow{100-130^\circ} (C_3H_5)_2BN(C_2H_5)_2 + C_3H_6.$$

When *p*-phenylenediamine is heated with *p*-vinylphenylboronic acid, the product is 2-(4-vinylphenyl)-1,3-dihydrobenzo[2,1,3]boradiazole[63].

Derivatives of bis(dihydrobenzo)boradiazole have been prepared in analogous fashion from *p*-phenylenediamine and 2,2′-tolandiboronic acid[71]. Treatment of 2-chlorovinylboron dichloride with ammonia in dry ether or benzene gave *BBB*-tri-(2-chlorovinyl)borazole[120]. *BBB*-Triallyl-*NNN*-trimethylborazole was prepared from *BBB*-trichloro-*NNN*-trimethylborazole and allylmagnesium bromide[121]. Unsuccessful attempts were made to prepare *BB*-diallyl-*B*-chloro-*NNN*-trimethylborazole and *B*-allyl-*BB*-dichloro-*NNN*-trimethylborazole by this reaction[121]. Groszos and Stafiej[122] prepared *BBB*-triallyl-*NNN*-triphenylborazole from *BBB*-trichloro-*NNN*-triphenylborazole and allylmagnesium bromide. The same compound is obtained using allyllithium[123]. The asymmetric borazole *NNN*-triphenyl-*B*-phenyl-*B*-methyl-*B*-allylborazole, which is stable towards moisture, was recently prepared[123]. By using *NNN*-triphenyl-*BBB*-trialkylborazole (where alkyl represents phenyl or methyl radicals or a hydrogen atom), the alkyl group on the boron atom can be replaced by the allyl group by reaction with allyllithium[124].

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THE PROLONGATION OF THE ACTION OF PHARMACEUTICAL PREPARATIONS BY MIXING OR COMBINING THEM WITH POLYMERS

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In the past decade considerable progess has been made in work on prolonging the action of pharmaceutical preparations. By the use of long-acting compounds, not only can the total amount of a preparation introduced into the body during a course of treatment and the number of doses or injections be reduced, but there are also other substantial advantages. Variations in the blood and tissue concentration of an active compound, which are unavoidable with periodically repeated doses of ordinary preparations, can be reduced or eliminated by the use of long-acting preparations; a constant concentration of the active compound that does not exceed the therapeutic dose, as frequently occurs with ordinary preparations, can be maintained with these long-acting preparations[1-4]. Their use also reduces the probability of unwanted effects, if the patient neglects to take medicine at the right time. Long-acting preparations should rapidly establish the required concentration of active compound in the blood and tissues; if this is not possible an ordinary preparation must be used at the beginning of a course of treatment so as to produce a rapid rise of concentration in blood and tissue. Moreover, the use of long-acting preparations saves much routine time; for example, a single dose or injection may replace four or five; this is of great practical importance in treatment in clinics.

The following methods may be used to prolong the action of pharmaceutical preparations: (1) introduction of various substituents into the molecule to retard the rate of excretion; (2) preparation of complexes or salts of pharmaceutical preparations with low-molecular-weight compounds; (3) use of special compounded preparations; (4) administration as a mixture with polymers; (5) formation of compounds with polymers.

The preparation of special long-acting compounded preparations and the use of these compounded preparations in medical practice have been dealt with in a number of reviews[2-7]. However, there are no systematic reviews on long-acting preparations made by methods (4) and (5). The present review is intended to fill this gap.

In the USSR, work in this field has been initiated by Ushakov and coworkers, who have worked on this problem over a long period, and also by Mokhnach, who has prepared and examined complexes of iodine with various polymers.

ADMINISTRATION OF PHARMACEUTICAL PREPARATIONS IN MIXTURES WITH POLYMERS

The action of many pharmaceutical preparations may be prolonged by administering them simultaneously with polymers; for example, procaine, morphine, insulin, adrenaline, antibiotics, and other preparations may be administered with polyvinylpyrrolidone[8-16]. However, the mechanism of action of polyvinylpyrrolidone has not yet been elucidated. Sheinaus and Sperandio[11] studied the effect of polyvinylpyrrolidone on the *in vitro* antibacterial action of 26 compounds against *M. pyogenes* var. *aureus*; the compounds included antibiotics, quaternary ammonium salts, phenols, mercury compounds, dyes, etc. Polyvinylpyrrolidone did not reduce the antibacterial activity of most of the preparations, but it did reduce the activity of iodine and zinc sulphate.

Malek and Kol'ts[17] showed that the rate of excretion of streptomycin and neomycin is reduced when the antibiotic is given mixed with heparin; the penetration of the antibiotic into lymph is also increased. This effect is explained by the formation of a salt of the antibiotic and heparin in the body.

It has also been shown[18] that the addition of polygalacturonic acid to the tannates of codeine, atropine, or morphine retards the excretion of these compounds; the retardation appears to be due to the formation of salts of polygalacturonic acid in the body. In a number of cases a polymer administered simultaneously with the pharmaceutical preparation increases its solubility and lowers its toxicity[16,19,20]; for example, heparin lowers the toxicity of polymyxin, streptomycin, and neomycin[17].

LONG-ACTING PREPARATIONS CONSISTING OF COMPOUNDS WITH POLYMERS

Long-acting preparations consisting of compounds with polymers may be divided into three groups: (1) complexes with polymers; (2) ionic compounds with polymers; (3) covalent compounds with polymers.

1. Complexes of pharmaceutical preparations with polymers. With many polymers iodine forms complexes possessing antimicrobial activity. Much work has been devoted to the preparation and study of iodine complexes of different polymers: polyvinylpyrrolidone[21-28], poly(ethylene glycol)[29], dextran[30], polyethoxypolypropoxyethanol[31], poly(vinyl alcohol)[32,33], and starch and its components[34-36]. The synthesis of iodine–polymer complexes, their properties, antimicrobial action, and field of application are discussed in detail in Mokhnach's monograph[37]. Mokhnach showed that the antimicrobial properties of coloured iodine–polymer complexes are due to the presence of the cation $I(I^+)$;[37-40] he also showed that the toxicity of iodine is reduced when it is combined with polymers.

Ushakov[41,42] has proposed a complex of iodine with polyvinyl alcohol ("iodinepolyvinyl alcohol") as a thixotropic gel which is melted for subcutaneous or intramuscular injection. Thixotropic gels of "iodinepolyvinyl alcohol" are prepared by cooling solutions of "iodineopolyvinyl alcohol" to which are added compounds (borax, boric acid) that form labile cross-links between the polymer macromolecules; these links are readily destroyed by heating and re-established at body temperature. The thixotropic gels melt at a temperature (usually 38–42°) which depends on the molecular weight of the polymer, its concentration in solution, and the number and kind of cross-links. To increase the iodine content of the gel and to prolong its absorption by the body[43,44], two-phase gels were prepared which contained an insoluble solid phase, consisting of an iodine complex of a three-dimensional copolymer of vinyl alcohol with diallylacetals or hydroxymethylcrotonamide, in addition to the "iodinepolyvinyl alcohol" thixotropic gel. Ordinary and two-phase gels of "iodinepolyvinyl alcohol" have been used in the treatment of tuberculosis, atherosclerosis, and other diseases.

Complexes of polyvinylpyrrolidone with halogen halides have been proposed as antiseptics; iodine monochloride and other halides have been used[19,45]. The preparation of iron–dextran complexes for the treatment of anaemia by injection has been described[46-48], and also the preparation of cobalt–dextran[49] complexes and complexes of polyhydroxyethylene-40-polystearate with various pharmaceutical preparations[50].

2. Long-acting preparations consisting of ionic compounds with polymers. Polymeric materials with ion-exchange properties have been used in the treatment of dermatitis, oedema due to cardiac insufficiency, kidney diseases, cirrhosis of the liver, and other diseases[51-56]. Blood anticoagulants, the preparation of which has been described, include sulphate esters of partially hydrolysed dextran[57-60], "dextranic acid"[61] (obtained as a by-product in the depolymerisation of dextran by an enzyme separated from *Asperigillus wentii*), glycogen, starch[62,63], xylan[64], chitin, chondroitin[65,66], sulphates and acetates of alginic acid[67], and carboxymethylcellulose[68]. Alkali metal salts of the sulphate esters of partially degraded polysaccharides have been proposed as haemostatics[69]. Dextran phosphates that increase the glucose content of the blood have been synthesised[70], and the synthesis of physiologically active amylose sulphate has been described[71].

Recently, the use of polymeric materials with ion-exchange properties, or ion-exchange resins, for the prolongation of the action of ordinary pharmaceutical preparations has been attracting increased interest. The salt of a pharmaceutical preparation and an ion-exchange resin is gradually decomposed in the organism and the liberated drug exhibits its therapeutic action. The decomposition of these salts in the gastro-intestinal tract may be represented by the following schemes:

in the stomach:

$$P\text{–}SO_3^-{}^+H_3N\text{–}A + HCl \rightleftharpoons P\text{–}SO_3H + A\text{–}NH_3^+Cl^-,$$

$$P\text{–}NH_3^+{}^-OOC\text{–}B + HCl \rightleftharpoons P\text{–}NH_3^+Cl^- + B\text{–}COOH;$$

in the intestine:

$$P\text{–}SO_3^-{}^+H_3N\text{–}A + NaCl \rightleftharpoons P\text{–}SO_3Na + A\text{–}NH_3^+Cl^-,$$

$$P\text{–}NH_3^+{}^-OOC\text{–}B + NaCl \rightleftharpoons P\text{–}NH_3^+Cl^- + B\text{–}COONa,$$

where P is the polymer and A and B are pharmaceutical preparations.

A large number of peroral long-acting drugs have been patented in Great Britain; these consist of salts of ion-exchange resins and various therapeutically and physiologically active compounds, including vitamins (thiamine, riboflavine, and pyrodoxine)[72], alkaloids (morphine, ephedrine, normorphine, dihydromorphine, and dihydromethylmorphine)[72-75], lucanthone[76], barbiturates[74,77], and

salicylates [77,78]. These preparations are known under the general name "resinates". Drugs with basic groups are usually combined with a sulphonated copolymer of styrene and divinylbenzene, or with a copolymer of divinylbenzene and acrylic or methacrylic acid or maleic anhydride, but other cation-exchange resins may also be used [79]. Combination of a drug with a polymer containing ionogenic groups may eliminate an unpleasant odour and taste as well as prolonging the action of the drug. Becker and Swift [80] have shown that some resinates are less toxic than the unmodified compounds.

A long-acting preparation of adrenocorticotropic hormone (ACTH) with enhanced activity may be obtained by interaction of the hormone with modified proteins (gelatin, albumin, globulin) [81]. A long-acting ACTH preparation has also been obtained by interaction of ACTH with hyaluronic acid [82]. Salts of polyuronic acids and choline, calcium, iron, magnesium, and cobalt have been proposed for the treatment of diseases of the liver, arteriosclerosis, and disorders due to the deposition of cholesterol in the vascular system [83].

According to patent information [84], long-acting antihistamine preparations may be obtained by the action of diphenylpyraline on sulphonated copolymer of styrene and divinylbenzene. Cobalt salts of carboxyl-containing polymers have been proposed for the treatment of dermatitis [85]. A mixture of polyacrylic acid cross-linked by polyhydroxy-compounds, and magnesium oxide, hydroxide, or carbonate has been proposed as an antacid to reduce the acidity of the gastric juice to pH 4–5 and maintain it at this level [86].

The preparation of salts of polysaccharide sulphates, used as anticoagulants, and aminobenzoic acid esters, used as local anaesthetics, has been patented [87].

Alkylsulphonated or acylated polymers containing basic groups, for example polyethylenimine [88], have been proposed for prolonging the action of pharmaceutical preparations and removing toxins from the body. Antibacterial compounds have been prepared by the interaction of quaternary ammonium bases with polysaccharides containing carboxy-groups, for example carboxymethylcellulose, carboxymethylstarch, and polyuronic acids [89].

Compounds containing ion-exchange resins and neomycin or sulphadiazine have been proposed for the treatment of skin diseases [90]. *In vitro* experiments have shown that the long-acting compounds have a greater antibacterial activity than the ordinary preparations.

Thus both natural and synthetic polymers are used to prolong the action of drugs. When synthetic polymers are used, their absorption and excretion is of great importance, but this has been little studied. Probably, it would be advantageous to use modified natural polymers such as polysaccharides and proteins.

Much work has been devoted to decomposition of salts of drugs and ion-exchange resins and to the liberation of drugs from the resins. It has been shown that 0.1 *N* hydrochloric acid very rapidly elutes drugs such as ephedrine and methapyrilene from cation-exchange resins containing carboxy-groups [1,91]. For this reason, many workers consider that polymers containing carboxy-groups cannot be used in making long-acting peroral preparations. The rate of decomposition of salts of drugs and polymers containing sulpho-groups in 0.1 *N* hydrochloric acid is much slower [1,91]; these polymers are therefore more useful for long-acting peroral preparations. Nash and Crabtree [92] have studied the liberation of tritium-labelled α-deoxyephedrine from these two types of cation-exchange resin in the body. It was found that the salt bond between α-deoxyephedrine and the polymer carboxy-groups is very rapidly destroyed in the stomach, but the liberation of α-deoxyephedrine from the sulphonated polymer is much slower. In the intestine the rate of liberation is the same for both types of polymer.

Smith *et al.* [91] studied the decomposition of a salt of methapyriline and a sulphonated copolymer of styrene with divinylbenzene in 0.1 *N* hydrochloric acid under static conditions. Chaudry and Saunders carried out analogous studies on ephedrine salts under static and dynamic conditions [1]. It was found that the rate of decomposition of both salts decreased as the particle size of the ion-exchange resin and the number of cross-links in the polymer increased, that is, as the total surface of the polymer particles and the rate of diffusion of acid in the polymer decreased. When a polymer with a large number of cross-links was used, the rate of elution of methapyrilene from the ion-exchange resin fell sharply as the particle size of the resin increased. The effect of the number of cross-links in the polymer on the elution rate decreases as the resin particle size is reduced. Under static conditions, when a salt of ephedrine and a cation-exchange resin was treated with 0.1 *N* hydrochloric acid, the rate of decomposition, and therefore the rate at which the ephedrine is liberated, decreased sharply after only two hours; at this point equilibrium is established between the ephedrine in solution and ephedrine bound to the sulpho-groups of the copolymer. When a sulphonated polymer containing ephedrine is treated with 0.1 *N* HCl under dynamic conditions, the sharp reduction in the rate of ephedrine liberation is not observed. In the presence of a polymer with free sulpho-groups the elution of ephedrine from resin under dynamic conditions is much slower. According to Chaudry, if a polymer with free sulpho-groups is added to a polymer containing ephedrine bound by saltlike bonds, a constant rate of ephedrine liberation in 0.1 *N* HCl can be achieved under dynamic conditions; this is a good model of the process occurring in the gastro-intestinal tract.

Chaudry and Saunders showed also that a salt of ephedrine and a sulphonated copolymer of styrene and divinylbenzene decomposes at about the same rate in 0.1 *N* solutions of hydrochloric acid, sodium chloride, or sodium bicarbonate. Swift [93], who studied the action of four antihistamine resinates on guinea-pigs, showed that the degree of prolongation depends on the particle of the resin; for example, granulated phenyltoloxamine and pyrilamine resinates were unsatisfactory, but the powdered resinates gave good results.

The rate at which a salt formed from a drug and an ion-exchange resin decomposes, and therefore the rate at which the drug is liberated, depends entirely on the presence of ions and is independent of the action of enzymes, peristalsis, or other physiological factors [94]. Since the total concentration of ions in the gastric juice changes within very narrow limits, the rate of liberation of drugs from ion-exchange resins in the gastro-intestinal tract must be fairly constant. The liberation of drugs from tablets and granules with special coatings cannot be uniform, since the decomposition of the coatings depends on a number of physiological factors [94]. Experiments *in vivo* have shown that, when acetylsalicylic acid and amphetamine resinates are administered, the rate of excretion of the drugs in the urine is much lower than when the same

drugs are given not combined with polymers[95,96]. It has been shown that the breaking of the salt bond between amphetamine and a cation-exchange resin proceeds at a constant rate[97]. Experiments on dogs and rabbits have shown that amphetamine resinate is more long acting than amphetamine sulphate in specially coated tablets[98,99]. With amphetamine resinate the daily therapeutic dose is much lower, and the curative effect much greater, than that obtained with ordinary amphetamine[99].

Methapyrilene resinate has about the same therapeutic activity as methapyrilene hydrochloride[91] Experiments *in vivo* showed that a salt of methapyrilene and a sulphonated copolymer of styrene and divinylbenzene had an action lasting 6.5 h, compared with 5.5 h for methapyrilene hydrochloride; there was therefore no significant increase in duration of action.

Malek[100,101] has prepared long-acting compounds by reacting antibiotics containing basic groups, like streptomycin and neomycin, with polymers containing acid groups (polyacrylic acid, polysaccharide sulphates and phosphates, polyuronic acids, and carboxymethylstarch). With these long-acting preparations a high concentration of antibiotic in the lymph was achieved; they were therefore termed "antibiolymphins".

It has been shown[100] that 75% of streptomycin given intravenously to rabbits is excreted in 8 h; the corresponding figure for the salt of streptomycin with dextran sulphate was 22.7%, and for the salt with polymethacrylic acid 45.5%. The toxicity of the long-acting preparations was lower than that of the free antibiotics.

Ushakov and Panarin[102] prepared salts of benzyl- and phenoxymethyl-penicillin with a copolymer of vinyl alcohol and vinylamine; these contained 11.22% of benzylpenicillin and 13.6% of phenoxymethyl-penicillin. The salts were not decomposed by dissolution in water and reprecipitation, and their solutions were stable. Preliminary biological tests at the First Leningrad Medical Institute showed that the benzylpenicillin polymer has the same activity (on a penicillin content basis) against *Staphylococcus* 209-R as standard benzylpenicillin. Thixotropic gels, with a setting temperature of 38–39°, of both polymers were prepared by a method previously described[41,42].

Brudney[103] showed in *in vivo* experiments that when penicillin V resinate is administered, a constant concentration of the active drug is maintained in the body for 3 h, after which there is a gradual fall in concentration. When free penicillin V is administered a high concentration in the body is obtained, which falls in a short time. The use of resinates of octanoic acid and undecenoic acid in intestinal affections has been described[104].

The work reviewed shows that a considerable number of long-acting drugs have been synthesised by linking ordinary drugs to polymers by ionic bonds. However, the literature contains insufficient systematic results of pharmacological and clinical trials of these long-acting preparations.

3. Long-acting pharmaceutical preparations consisting of covalent compounds with polymers. When compounds bound covalently to polymers are introduced into the body, they can act in two ways: (a) the covalent bond between the polymer macromolecule and the drug molecule is gradually destroyed and the drug beings to exercise its therapeutic action; (b) the covalent bond is maintained and the therapeutic action is due to the polymer-drug compound.

The therapeutic effect of a drug is due to its structure, that is, to the presence in its molecule of certain functional groups and of different substituents in positions related to these groups. Therefore, if the covalent bond between the drug and the polymer is maintained in the body, the addition of the drug to the polymer should not destroy or reduce its therapeutic effect.

Ushakov[105] has proposed the modifications of drugs by combining them with polymers used as blood substitutes. Different copolymers of vinylpyrrolidone and vinyl alcohol with crotonic acid, hydroxymethylcrotonamide, and vinylamine were synthesised. The presence in these copolymers of hydroxy-, amino-, carboxy-, and hydroxymethylcarbamoyl groups enabled a number of drugs to be combined with their macromolecules. By the use of these blood-substituent polymers, a number of drug polymers were prepared for the treatment of cardiovascular diseases, tuberculosis, and tumours[102,106–110]. As Ushakov[106] has shown, the drug can also be introduced into this type of macromolecule by copolymerising vinylpyrrolidone with organic drugs containing unsaturated groups.

By reacting polyvinyl alcohol with the lactone of di-(4-hydroxycoumarin-3-yl)acetic acid (pelentanoic acid), Ushakov and Kononova[107,108] synthesised the ester of pelentanoic acid, which is a blood anticoagulant. The ester of pelentanoic acid with the copolymer of vinyl alcohol and vinylpyrrolidone was obtained in the same way. The esters of pelentanoic acid with polyvinyl alcohol dissolve readily in water to form stable solutions and have blood-substituent properties. Trials on rabbits and dogs at the Leningrad Blood Transfusion Institute showed that intravenous administration of an aqueous solution of the ester of pelentanoic acid with polyvinyl alcohol rapdily lowers the blood prothrombin and maintains it at a low level for a considerable time[107]. The hydrogen sulphate esters of polyvinyl alcohol, which are also anticoagulants, were prepared[106] by the reaction of polyvinyl alcohol or polyvinyl acetate with sulphuric or chlorosulphonic acid.

Drug polymers with antitubercular activity have been obtained[109] by the action of *p*-aminosalicyloyl chloride on polyvinyl alcohol. These compounds contained up to 30% of *p*-aminosalicylic acid and had blood-substituent properties. Trials showed that the rabbit excreted the preparation much more slowly than ordinary PAS. *In vitro* tests on Petran'yani's medium showed that the preparation had an antimicrobial activity against *Mycobacterium tuberculosis*. Thixotropic gels of the preparation, setting at 38–40°, were obtained by a method previously described[42,44].

Blood-substituent polymers with antisclerotic action have been prepared by copolymerising vinylpyrrolidone with vinyl oleate. When the product was introduced into the blood, a fall in cholesterol content was noted and also partial "washing away" of sclerotic platelets, but it was found that the polymer was deposited in the liver and spleen of the experimental animals; the authors consider that this deposition is due to the long side chains. Blood-substituent polymers with antitumour activity and antioxidant properties were obtained by copolymerising vinylpyrrolidone and vinylhydroquinone[110], and also by acetylating polyvinyl alcohol with salicylaldehyde[106].

Jatzkewitz[111,112] combined glycylleucylmescaline with a copolymer of vinyl pyrrolidone and acrylic acid by means of an amide bond. When the product was given subcutaneously to experimental white mice, mescaline was observed in the urine for 17 days; in contrast, mescaline was

eliminated in 16 h when it was given as mescaline hydrochloride, as glycylleucylmescaline hydrochloride, or as a mixture of the copolymer of vinylpyrrolidone and acrylic acid with mescaline. It should be noted, however, that the high-molecular-weight product was more toxic than free mescaline. According to Jatzkewitz, the increased toxicity is due to the presence in the polymer used of a fraction with a very high molecular weight. Later Jatzkewitz[113] proposed other compounds in which physiologically or therapeutically active compounds are linked by an amide bond to the copolymer of vinylpyrrolidone and acrylic acid; the drugs used included 5-hydroxytryptamine, tryptamine, histamine, thyroxine, antibiotics with a free amino-groups, and hormones.

Kratzl and Kaufmann[114] obtained an acetylsalicylic ester of starch containing up to 0.7 acetylsalicylic acid residues by the action of acetylsalicyloyl chloride on soluble starch in the presence of potassium hydroxide. A higher degree of esterification is obtained when pyridine is used but the product is difficult to purify. Labelled ^{14}C was used in the synthesis of this acetylsalicylic ester. The breakdown of the ester was studied in dogs and rabbits[115]. The animals received an intramuscular solution of the ester in glycerol-acetonide and the concentration of acetylsalicylic acid in the blood was determined colorimetrically and radiometrically. It was found that administration of the starch ester gave a concentration of acetylsalicylic acid in the blood 20 times lower than that obtained when the free acid was administered. A vanillin diethylamide derivative of starch carbonate, with two ester residues per unit link[116], was obtained by the action on soluble starch of the product of the reaction between phosgene and vanillic acid diethylamide; the diethylamide was labelled with ^{14}C. Intramuscular administration of the product in glycerol-acetonide gave a much lower concentration of vanillic acid diethylamide in the blood than when an equivalent amount of the free diethylamide was administered. It was therefore shown that only slight cleavage occurs when the starch derivatives are given intramuscularly.

Compounds with antitubercular activity have been prepared by condensing polysaccharides, oxidised with sodium metaperiodate, with thiosemicarbazide, aminobenzaldehyde thiosemicarbazone, and isonicotinic acid hydrazide[117-119]. Starch, alginic acid, and inulin have been used in the preparation of high-molecular-weight pharmaceutical preparations.

Long-acting drugs have also been prepared by condensing compounds containing an amino-group with the aldehyde groups of partially oxidised dextran[120]. A nicotinic acid ester of starch that liberates the free acid in the body has also been described[121].

The work reviewed here shows that the prolongation of the action of drugs by administering them mixed with, or combined with, polymers is attracting the attention of a wide circle of research workers throughout the world. There is no doubt that systematic studies in this field will lead to new valuable long-acting preparations.

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PHYSICOCHEMICAL FEATURES OF THE SPREADING OF A LIQUID METAL ON A SOLID METALLIC SURFACE

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1. INTRODUCTION

The interaction between metallic melts and solid metals is a complicated physicochemical problem, whose scientific and industrial importance has recently been stressed by the growing use of liquid metals in many areas of present-day technology. Liquid metals are used as heat-transfer media in rocket propulsion units and in nuclear power stations; they are used in soldering and in welding, in the deposition of protective metallic coatings, in the manufacture of metalloceramic objects, in the extraction of noble metals from ores by the amalgamation method, and in many other technological processes.

When a liquid metal is brought into contact with a solid, more refractory metal, various physicochemical processes can take place: corrosion[1-7], embrittlement resulting from adsorption and the large decrease in free energy at the interfacial boundary between the melt and the metal[8-17], etc. The spreading of metallic melts on solid metal surfaces plays a very important role in all these processes. In addition to purely surface spreading, the atoms of the melt can penetrate into the bulk of the solid metal by normal (volume) diffusion and also by diffusion along grain boundaries and other structural defects. Volume diffusion in metals has been investigated in detail and is discussed in a number of monographs and review articles[18-22], but surface spreading problems have until recently attracted far less attention in spite of their fundamental importance.

The present review presents the results of recent theoretical and experimental studies on the kinetics of spreading of liquid metals on the surface of higher-melting metals, in the absence of extraneous (external) motive forces, such as hydrostatic pressure, gravity, etc. Measurements of contact angles, which apply to static situations under conditions of incomplete wetting, and the set of problems associated with self-diffusion, will not be considered, because they are adequately discussed elsewhere[23-31].

Liquid metals can spread on solid metal surfaces by surface diffusion, *i.e.* by the migration of atoms from the melt.

Diffusion processes are described mathematically by Fick's laws[18], which state that under a particular set of conditions diffusional spreading should be proportional to $t^{1/2}$, where t is time measured from the beginning of the process. The rate of spreading of a substance under those conditions is characterised by the surface diffusion coefficient D_s, which increases exponentially with temperature.

The mobility of atoms on a solid surface was first demonstrated experimentally by Volmer[32-34]. Systematic studies of the diffusion of one metal on the surface of another metal were undertaken during research on electronic valves with activated cathodes. The electron work function is significantly decreased when a refractory metal cathode is covered with a monolayer of an alkali metal[35]; measurements of the thermionic emission of electrons therefore provide information on the rate of surface diffusion of atoms. Thus, it has been shown that Na, Ba, Cs, and Th atoms can migrate on the surface of tungsten[36-41]; a similar phenomenon has been observed[42] when barium is deposited on molybdenum.

Interesting data on the mobility of atoms on solid metallic surfaces have been obtained by an electron gun technique[43]: in particular, studies of the diffusion of barium on a tungsten surface[44-46] have shown that adsorption of oxygen can arrest the spreading of barium[47].

It has been possible to observe surface diffusion microscopically under strong enough magnification: the migration of copper atoms on silver has been shown, by this method, to produce agglomerates on surface defects[48].

Radioactive isotopes have also been applied to the determination of surface diffusion coefficients (spreading of polonium on silver[49] and platinum[50], and of copper on silver[51]).

The experimental results of the above work were used to evaluate the surface diffusion coefficients D_s and their temperature variation: satisfactory agreement with experiment is usually given by an expression of the type $D_s = D_{s_0} \exp(-U_s/kT)$, where D_{s_0} is a constant and U_s the activation energy for surface diffusion. According to the Frenkel' model[52], the activation energy is a measure of the work needed to remove an atom from its rest position. Surface diffusion necessitates the rupture of fewer interatomic bonds than does volume diffusion, and activation energies for surface diffusion are accordingly lower than those for volume diffusion.

The high mobility of atoms in the layer of solid metal immediately below the surface is confirmed also by the observed smoothing of surface scratches[53]. Geguzin and his coworkers have shown[30,54] that the diffusional transport of matter is facilitated (in comparison with volume diffusion) not only on the purely "geometrical" surface of a solid, but also within a layer adjacent to the surface whose thickness may reach several hundred interatomic spacings in real solids.

Observations of the diffusion of mercury on various metal surfaces are particularly interesting, because diffusion in this case occurs fairly fast even at relatively low temperatures.

Tammann[55] studied the migration of mercury on silver, gold, copper, tin, lead, zinc, and cadmium surfaces; typically, the spreading of mercury was accompanied by the formation of a dull patch which could be easily seen[59].

The spreading of mercury on the surface of tin[56,57] involves chemical reaction with the solid metal[58]. The activation energy for the Sn–Hg diffusion couple has been shown to decrease as the surface of the specimen is made progressively more imperfect by deformation[58].

Studies of the diffusion of mercury on the basal planes of zinc and cadmium single crystals have revealed diffusion anisotropy[21,60], *i.e.* a variation of the rate of the process with crystallographic direction.

Thus, the experimental evidence for the ability of various metal atoms to diffuse on a solid metal surface at appreciable rates is quite convincing†. We should also note, however, that most of these investigations amount to

† We reject as unfounded Heumann and Forch's conclusion[61] that liquid metals cannot spread on solid metal surfaces by diffusion. (Those workers claim that a liquid metal can spread only in the capillary gap between the surface of the metal itself and a layer of oxide or other similar surface film.)

no more than disconnected observations, and that their results have not yet been unified into a general picture of the many different processes involved in the migration of metallic melts on solid metal surfaces.

In recent years a systematic study of the surface spreading of liquid metals has been carried out in the Colloidal Chemistry Department of Moscow State University. The results of this work will be presented below.

Section 2 deals with the possibility of two radically different modes of spreading of melts on a solid surface (wetting and surface diffusion), depending on the microprofile of the experimental surface. The basic kinetics of the wetting of a zinc surface by mercury are discussed in Section 3, whilst the influence of volume diffusion on the course and outcome of the wetting process is considered in Section 4. Section 5 is devoted to the diffusional spreading of mercury and gallium on a zinc surface.

2. INFLUENCE OF THE MICROPROFILE OF THE SOLID SURFACE ON THE SPREADING OF A LIQUID METAL

When analysing the behaviour of a liquid on a solid surface, one usually considers the relationship between the quantities σ_s, σ_l, and σ_{sl}, where σ_s and σ_l are the specific surface free energies of the solid and the liquid at their interface with the experimental medium, and σ_{sl} is the free energy at the solid–liquid interfacial boundary.

It is usually assumed that, if

$$\sigma_s > \sigma_{sl} + \sigma_l, \tag{1}$$

complete wetting occurs, *i.e.* a drop of the liquid will spread on the solid surface as a film of ever-decreasing thickness.

In the opposite case, *i.e.* if

$$\sigma_s < \sigma_{sl} + \sigma_l, \tag{2}$$

the resulting drop has a finite angle of contact. Under these conditions the liquid metal can only spread by surface diffusion.

Thus, even an analysis of the conditions for wetting leads to the conclusion that the spreading of a liquid on a solid surface can occur, in principle, by two qualitatively different processes: wetting (the viscous flow of a continuous surface phase) and surface diffusion (the migration of atoms)[62].

However, inequalities (1) and (2) are applicable only to ideally smooth solid surfaces[63–65]. Since all real solid surfaces have their own, characteristic microprofile, the spreading of liquids can only be described correctly if surface geometry is taken into account as well as the physical properties of the system.

Rebinder[63] also considers the frictional force acting on the periphery, whose magnitude depends on the degree of roughness of the surface. This force opposes the motion of the front of the spreading drop, and causes the angle of contact of the advancing front to be greater than that of the receding front (wetting hysteresis). Deryagin[64], in his theoretical study of the effect of the microprofile on the contact angle θ, concluded that a liquid can wet a rough surface along microdepressions and grooves if $K\cos\theta \geqslant 1$ (where K is the roughness coefficient, *i.e.* the ratio of true to apparent surface area, and θ is the angle of contact on an ideally smooth surface).

It follows from the condition $K\cos\theta \geqslant 1$ that, if the contact angle on an ideally smooth surface is acute, (*i.e.* if $\cos\theta > 0$) it should always be possible, in principle, to produce a degree of roughness sufficient to allow the liquid to wet the surface.

These views are clearly illustrated by the following model. Consider a longitudinal groove on a solid surface, whose cross-section is an isosceles triangle of vertex angle φ (Fig. 1*a*). Assume that the given liquid makes an angle of contact θ on a smooth surface of the given solid, which is acute‡. In the absence of extraneous forces, wetting is thermodynamically possible if it involves a decrease in the free energy of the system.

For our prescribed geometry, wetting along the groove will occur if

$$\sigma_s b > \sigma_{sl} b + \sigma_l b(\sin\varphi/2). \tag{3}$$

Since for the ideally smooth surface $\sigma_s - \sigma_{sl} = \sigma_l\cos\theta$, we obtain the following condition for wetting to occur along the groove:

$$\varphi < 180° - 2\theta. \tag{4}$$

Thus, expression (4) defines the critical value of the re-entrant angle φ at the vertex of a microgroove on a solid surface, corresponding to the transition from one type of surface migration (diffusion) to the other (viscous flow).

The decrease in surface energy ($\Delta\sigma$) accompanying wetting can be computed as follows.

Allowing for the microprofile of the solid surface (Fig. 1*b*), we have

$$\Delta\sigma = K\sigma_s - (K\sigma_{sl} + \sigma_l). \tag{5}$$

Under static conditions (drop at rest on a smooth surface), $\sigma_s - \sigma_{sl} = \sigma_l\cos\theta$. Hence,

$$\Delta\sigma = \sigma_l(K\cos\theta - 1). \tag{6}$$

All the quantities appearing in Eqn. (6) can be measured experimentally. The surface tension σ_l is known over a wide temperature range for many liquids, including molten metals[66], and reliable methods are available[67,68] for the measurement of contact angles θ.

The roughness coefficient K can be obtained with the help of microprofile traces for solid surfaces, which enables the roughness factor to be calculated as the ratio of the true to the "geometric" surface area.

Thus, by analysing the effect of the microprofile of a solid surface upon its interaction with a liquid, we can

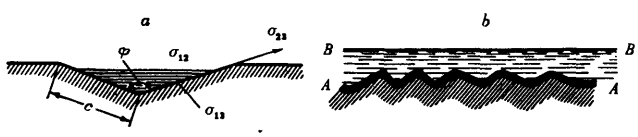

Fig. 1. *a*) Condition for wetting along a groove; *b*) diagram for calculating $\Delta\sigma$. *AA* is the solid surface and *BB* the liquid surface.

‡ When $\theta > 90°$, the product $K\cos\theta$ is negative, and wetting is impossible.

show that liquids which form drops of small contact angle on a smooth surface can wet a rougher surface of the same solid material.

This conclusion was confirmed by the writer[62] in an investigation of the spreading of mercury on an oxide-free zinc surface§, when both types of spreading (wetting and surface diffusion) were observed for the first time on a single solid–liquid couple, depending on the degree of microroughness.

On a smooth surface of purity class 9 (Fig. 2*a*), mercury forms a drop of $\sim 7^\circ$ contact angle. A circular, dull patch grows around the drop at a rate which follows the time law characteristic of diffusion processes ($r \propto t^{0.5}$, where r is the radius of the spot and t is time).

On a rough surface of purity class 6 (Fig. 2*b*), the spreading of mercury takes on an entirely different character. The mercury does not form a drop with a finite angle of contact, and it spreads much faster than in the previous case as a flat circular spot whose radius r increases as $r \propto t^n$ (where $n \simeq 0.27$).

The effect of the microprofile on the spreading of mercury was further studied using zinc plates whose surfaces had been subjected to different types of chemical or mechanical treatment. These included prolonged (several days) and brief (several minutes) etching in 10% NH_4OH solution, 10 minutes' etching in 12% HNO_3, electropolishing (both vigorous and mild), lapping on emery and polishing on cloth, etc.

The microprofile curves obtained with these specimens showed that, irrespective of the method of surface preparation, wetting occurs whenever the microgrooves on the surface have a re-entrant angle of $\sim 160^\circ$ or less. On smoother surfaces (re-entrant angles $\geqslant 166^\circ$), mercury spreads only by diffusion. These results are in satisfactory agreement with Eqn. (4)¶.

The critical part played by the microprofile was confirmed also by the following experiments. Using a special tool, longitudinal grooves of triangular profile and different dihedral angles were scratched on a smooth zinc surface. Residual stresses were removed by lightly annealing the specimens. A mercury droplet was then deposited in one of the grooves under a 10% solution of ammonia. Flow of the mercury by wetting along the groove was observed only when the angle at the apex of the groove was less than 160°, which is in satisfactory agreement with Eqn. (4) in view of the uncertainties in the measurement of the contact angle for mercury and of the angle φ.

Fig. 2. *a*) Microprofile of zinc plates with smooth surface (purity class 9); *b*) microprofile of zinc plates with rough surface (purity class 6).

These results show that we must clearly distinguish two qualitatively different mechanisms for the spreading of a liquid metal on an oxide-free solid metal surface: surface diffusion and wetting. Surface diffusion is observed when the contact angle is large; wetting occurs when the contact angle is relatively small and the surface has an appreciable roughness. These two processes, which we have observed in a single (mercury–zinc)† system, have fundamentally different mechanisms as well as showing differences in quantitative behaviour.

3. KINETICS OF WETTING OF A ZINC SURFACE BY MERCURY

Most of the experiments on the wetting behaviour of mercury have been performed on polycrystalline nickel plates 1.8 mm thick, at room temperature[71-72]. The microprofile required to cause wetting was produced by etching in 12% HNO_3 for 10 min. The etched plates were rinsed in a stream of water and immersed in a bath containing a 10% solution of ammonia for the duration of the experiment‡.

One series of experiments was performed with square plates held horizontally. A small droplet of mercury (varying from a few tenths of a milligramme to tens of milligrammes) was deposited at the centre of the plate: thus, the experimental conditions were those of the two-dimensional problem with a "point" source of finite capacity (or, more precisely, a source of small, finite radius). As soon as the mercury comes into contact with the zinc surface, it begins to spread in three consecutive stages.

The first and shortest stage (a fraction of a second) consists in rapid wetting under the combined influences of capillary forces and the weight of the drop: the drop takes the form of a small "puddle" with a mirror-bright surface whose size depends on the mass of mercury (usually not more than 3–4 mm radius for a weight of mercury of the order of 10 mg).

Immediately after this rapid first stage, the second, main stage begins. A truly circular matt spot, bright and easy to see, and with a sharply defined front, begins to spread outwards from the edge of the shiny puddle§. Initially, the front of the spot moves at about 1 cm s^{-1}, the speed decreasing according to a definite law. The dull spot with a mirror-bright puddle at its centre can be observed for a relatively short time: after a few minutes, the centre of the spot loses its specular appearance, but the spot itself continues to grow as before.

The increase in spot radius r with time t is shown in Fig. 3*a*, for which observations were started a few seconds after the onset of the second stage. The main stage of the

§ These experiments were made on polycrystalline zinc plates (98.7% Zn); the medium used to dissolve the oxide film during the experiments was always a 10% solution of ammonia.

¶ There are also some interesting data[69] on the existence of microprofile in other metals. The mean angle of the microgrooves after polishing or chemical etching is usually $\sim 168^\circ \pm 2^\circ$.

† Heumann and Forch[70], who studied the mercury–gold couple, also report that the liquid metal will wet a sufficiently rough solid surface.

‡ Practically the same results are obtained if 5% NaOH or 2% HCl are used to dissolve the oxide film on zinc.

§ The position of the front of the spot as determined visually is almost indistinguishable from that determined autoradiographically in control experiments with the radioactive isotope ^{203}Hg.

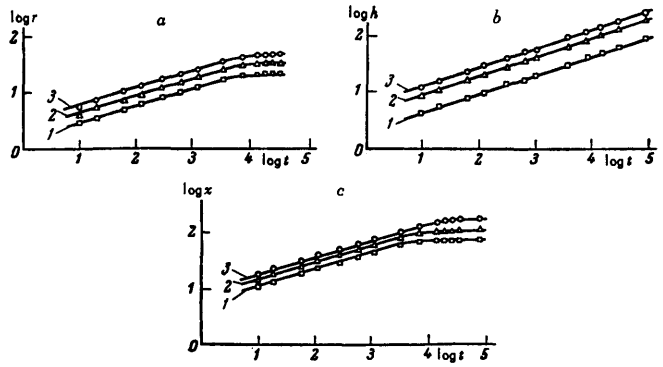

Fig. 3. *a*) Variation of the radius r (mm) of a mercury spot with time t (seconds) for different masses (m) of the mercury drop: 1) 1 mg; 2) 5 mg; 3) 10 mg;
b): 1) variation of the height h (mm) to which the mercury spreads on a vertical zinc plate with time t (seconds); 2) and 3) ditto, for plates inclined at 22° and 10° to the horizontal;
c) variation of the distance x (mm) to which the mercury spreads, in each direction, along a channel 1 mm wide with time t (seconds) for different masses (m) of the mercury drop: 1) 1 mg; 2) 2 mg; 3) 3 mg.

process is described by the power law¶ $r = A_2 t^{n_2}$, where the exponent n_2 is found to be independent of the mass of mercury m, and equal to ~ 0.27 in all experiments, whereas the coefficient A_2 increases with the mass of the drop:

m	1	5	10
A_2	1.5	2.3	2.75

when m is in milligrammes, r in millimetres, and t in seconds.

Now begins the third stage, in which the rate of growth of the spot falls off rapidly. The linear variation of the logarithm of the spot radius with the logarithm of time, which characterises the second or main stage, ceases to apply, and after a time varying from half an hour to several hours — depending on the initial weight of mercury — the growth of the spot practically ceases.

Before the results can be analysed, we must first establish qualitatively whether the spreading in this case occurs by surface diffusion or by wetting. The answer is given quite unambiguously by experiments on the effect of gravity.

Thus, if the upward spreading of the liquid on a surface inclined to the horizontal at an angle γ involves a layer of finite thickness, the rate of spreading should decrease with increase in the angle γ. If, on the other hand, diffusion alone is involved, the rate of the process should be independent of the inclination of the specimen.

Experiments of this type were performed on narrow zinc plates 2–2.5 cm wide and up to 30 cm long. The lower edge of the plate was immersed in a large mercury pool, so that the relative change in the mass of mercury during the experiment could be neglected. This arrangement provided a linear source of "infinite capacity", corresponding to the problem of one-dimensional spreading of mercury.

¶ Throughout this paper, the subscript 2 refers to the two-dimensional (or circular) case, and the subscript 1 to the one-dimensional (or linear) case.

As soon as the zinc plate touched the mercury, a dull spot with a sharply delineated front began to spread upwards at a rate described by the time law $h = A_h t^n$ for all values of the angle γ (Fig. 3*b*). The exponent $n = 0.32$ is independent of the slope angle, but the coefficient A_h increases very significantly as this angle is decreased:

γ	10°	22°	90°
A_h	5.5	4.3	2.1

when h is in millimetres and t in seconds.

Thus, these experiments confirm that mercury spreads on a roughened zinc surface by the viscous flow of a layer of finite thickness ("phase layer").

The linear (one-dimensional) spreading of mercury was examined as well as the circular spreading (two-dimensional problem). In these experiments the plates were covered with a thin layer of nitrocellulose varnish before being etched in nitric acid. While the lacquer was still tacky, a narrow "channel" 1 mm wide was scribed on the surface of the specimen with a wooden scriber. The mercury droplet was deposited at the centre of the channel under a layer of ammonia solution, and the movement of the matt front was observed. The spreading of the mercury over a long period of time was again found to be satisfactorily described by the power law $x = A_1 t^{n_1}$ (see Fig. 3*c*), the exponent n_1 being, as before, independent of the mass m of the drop ($n_1 \simeq 0.30$ for all the experiments). The coefficient A_1 increases with m:

m	1	2	3
A_1	6.3	7.6	9.1

when m is in milligrammes, x in millimetres, and t in seconds.

Thus, circular spreading is appreciably slower than spreading along a channel. This dependence of velocity on the geometry of the system is a further qualitative argument in favour of the wetting mechanism for the spreading of mercury on a rough zinc surface.

Another characteristic feature of the system is that practically no trace of matt areas can be found on the surface of the plate when the lacquer is removed (*e.g.* with acetone), except of course for the channel itself and a narrow region on either side of it. On the other hand, when mercury spreads on a metal surface by diffusion along, as on silver or tin, a lacquer film is no barrier to the spreading of the dull spot[55].

An approximate quantitative analysis of these observations will now be given, in which the motion of mercury on a zinc surface will be treated as the viscous, quasi-steady-state Newtonian flow of a continuous, three-dimensional layer ("phase layer"), the thickness of the layer gradually decreasing as the area of the mercury spot increases[73]. In the absence of extraneous forces, including gravity, this motion is possible if an increase in area of the spot is accompanied by a decrease in the total surface energy of the system. We shall also assume, to a first approximation, that the mass of the mercury film remains constant throughout the lengthy second stage.

Consider first the one-dimensional case, the spreading of a drop of mass m along a channel of width a (Fig. 4). We shall make the simplifying assumption that the wetting mercury film becomes uniformly thinner, *i.e.* that at any time t the thickness of the layer $z(t)$ is the same at every point.

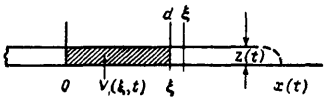

Fig. 4. Calculation of the viscous drag on a mercury film.

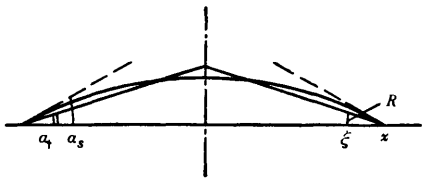

Fig. 5. Approximation to the profile of a mercury layer.

Let the position of the mercury front be $\pm x$ at time t since the beginning of the experiment. The layer thickness will then be $z(t) = m_1/x\delta$, where δ is the density of mercury, and $m_1 = m/2a$ is the mass per unit width of the channel. The volume of mercury between the cross-sections $\xi = 0$ and ξ (also, per unit width of channel) is $V_1(\xi, t) = m_1\xi/x\delta$. Therefore, the mean rate of flow at the cross-section ξ is given by

$$v(\xi, t) = -(1/z)\,\partial V_1/\partial t = (\xi/x)\,(dx/dt), \qquad (7)$$

i. e. it increases linearly from zero at $\xi = 0$ to a maximum of dx/dt in the region of the front of the spot. Assuming a constant velocity gradient throughout the thickness of the layer, we can use Newton's law to find the force due to viscous resistance acting on the element $d\xi$ (per unit width of flow):

$$dF = \eta\,[v(\xi, t)/(z/2)]\,d\xi = \eta\,(\xi/x)\,dx/dt\;2\,(x\delta/m_1)\,d\xi,$$

where η is the viscosity of mercury.

Integrating with respect to $d\xi$ from 0 to x, we obtain the total viscous force acting on the layer:

$$F = (\eta\delta/m_1)\,x^2\,(dx/dt). \qquad (8)$$

Let $\Delta\sigma$ be the decrease in the total specific surface energy, which causes the mercury drop to wet, and is numerically equal to the force "pulling" on the layer [see Eqn. (5)]. Equating the viscous retarding force of the mercury layer to the pulling force, and ignoring any acceleration, we arrive at the equation of motion of the mercury front:

$$\frac{1}{m_1}x^2\,dx = \frac{\Delta\sigma}{\eta\delta}\,dt. \qquad (9)$$

It follows that the motion of the mercury front along the channel should be described by the law

$$x = (3m_1\Delta\sigma/\eta\delta)^{1/3}\,t^{1/3}. \qquad (10)$$

Putting $\Delta\sigma/\eta\delta = \Sigma$, we finally obtain

$$x = (3m_1\Sigma)^{1/3}\,t^{1/3}. \qquad (11)$$

This approximate solution gives $n_1 = 1/3$ and $A_1 = (3m_1\Sigma)^{1/3}$. The value of A_1, however, is probably too high, since the thickness of the layer decreases from $z(t)$ to zero (or, more correctly, to a value of the order of atomic dimensions) in the region directly adjacent to the front of the spot. Since a full and rigorous solution of the problem, leading to an expression for the profile of the layer, presents considerable difficulty, the obvious first approximation is to assume that the profile can be represented by a circular arc based on a chord of length $2x$ and forming an angle of contact α_S† with the surface of the plate (see Fig. 5). This is just the shape which the drop should take up under static conditions if the angle of contact is finite and gravity forces can be neglected. Computation can be further simplified by replacing the segment with an isosceles triangle of equal area, when the "angle of contact" takes the value $\alpha_t \simeq 2/3\alpha_S$ (with this substitution, the solution obtained is practically indistinguishable from that given by the circular arc approximation to the profile).

In this model, the thickness of the layer at the cross-section ξ at any time is given by the expression $z(\xi, t) = 2(m_1/x\delta)(1 - \xi/x)$, and the volume of mercury between the cross-sections $\xi = 0$ and ξ (per unit channel width) is $V_1(\xi, t) = (m_1\xi/x^2\delta)(2x - \xi)$. Proceeding as before, we obtain the force of viscous resistance acting on the element $d\xi$. After integration, this gives

$$F = (\eta\delta/m_1)\,[\ln(2m_1/\lambda x\delta) - 1]\,x^2\,dx/dt. \qquad (12)$$

Since the thickness of the "phase layer" cannot be less than a few atomic layers, we take as the upper integration limit the distance $\xi = x - \lambda\cot\alpha_t = x - \lambda x^2\delta/2m_1$ (Fig. 5), where λ is the thickness of the layer at the edge of the spot (of atomic dimensions). The expression thus obtained differs from the previous one which referred to the flow of a layer of constant thickness, only by the factor $[\ln(2m_1/\lambda x\delta) - 1]$, which changes very slowly in the second stage of the process and can therefore be replaced by the constant coefficient $\kappa \simeq 7$–11 (these are the extreme values of κ for the range of m_1 and x values under discussion). Thus, the resulting equation $\bar{F} = \Delta\sigma$ differs from that previously obtained only by the constant factor κ: $(1/m_1)x^2dx = (\Sigma/\kappa)dt$. The solution is the expression

$$x = (3m_1\Sigma/\kappa)^{1/3}\,t^{1/3} = A_1t^{1/3}. \qquad (13)$$

The two-dimensional problem with a point-source of finite capacity can be solved by an analogous procedure. Assuming, as a first approximation, that the mercury layer has a constant thickness at any instant [given by $z(t) = m/\pi r^2\delta$, where $r = r(t)$ is the radius of the spot], we find the volume of mercury contained in a cylinder of radius ρ: $V(\rho, t) = (m/\delta)\rho^2/r^2$, where $r > \rho$. The mean rate of flow through the surface of this cylinder is

$$v(\rho, t) = -(1/2\pi\rho z)\,\partial V/\partial t = (\rho/r)\,dr/dt,$$

i. e. it increases linearly from the centre of the circle to the periphery. The force of viscous resistance acting on an elementary annulus of width $d\rho$ is

$$dF = \eta\,[v(\rho, t)/(z/2)]\,2\pi\rho\,d\rho = \eta\,(\rho/r)\,(dr/dt)\,2\,(\pi\rho^2\delta/m)\,2\pi\rho\,d\rho.$$

Integration of this expression with respect to $d\rho$ from 0 to r gives

$$F = (4\pi^2/3)\,(\eta\delta/m)\,r^4\,dr/dt.$$

Equating the viscous resistance force F to the tension $2\pi r\Delta\sigma$, acting on the edge of the mercury film, we obtain an equation of motion for the mercury front:

$$\frac{1}{m}r^3\,dr = \frac{3}{2\pi}\Sigma\,dt,$$

† Note that under dynamic conditions (in the presence of viscous flow) this angle cannot be zero, since this would imply infinitely large viscous forces.

TABLE 1.

Problem	Exponent n of time t		Exponent s of drop mass m	
	linear (n_1)	circular (n_2)	linear (s_1)	circular (s_2)
Theory	1/3	1/4	1/3	1/4
Experiment	0.30	0.27	0.32	0.26

TABLE 2.

Drop mass m, mg	1	2	3	5	10
A_1(theory), cm $s^{-1/3}$	0.43	0.54	0.61	—	—
A_1(expt.), cm $s^{-1/3}$	0.62	0.76	0.91	—	—
A_2(theory), cm $s^{-1/4}$	0.32	—	—	0.48	0.58
A_2(expt.), cm $s^{-1/4}$	0.15	—	—	0.23	0.27

whose solution is the power function of time

$$r = \left(\frac{6}{\pi} m\Sigma\right)^{1/4} t^{1/4}. \qquad (14)$$

As in the one-dimensional case, a better approximation to the shape of the wetting drop would be a spherical cap. Replacing this, as before, by a cone of equal volume, we obtain the following expression after integration with respect to $d\rho$:

$$\frac{1}{m} r^3 dr = \frac{3}{2\pi} \frac{\Sigma}{\kappa} dt.$$

Again, the logarithmic term can be replaced by a constant factor: $\kappa = \ln(3m/\lambda\pi r^2\delta) - 3/2 \simeq 7-11$. The final equation for circular wetting is

$$r = \left(\frac{6}{\pi} m \frac{\Sigma}{\kappa}\right)^{1/4} t^{1/4}. \qquad (15)$$

Thus, the parameters describing the second stage of the wetting process are: for a drop creeping along a "channel", $n_1 = 1/3$ and $A_1 = (3m_1\Sigma/\kappa)^{1/3}$; for circular wetting, $n_2 = 1/4$ and $A_2 = [(6/\pi)m\Sigma/\kappa]^{1/4}$.

Experimental and calculated values of the exponents for a drop of mass m and time t are compared in Table 1: it can be seen that the agreement is fairly good.

Comparison of the experimental and theoretical values of the coefficients A_1 and A_2 (Table 2) is particularly interesting.

The value of $\Delta\sigma$ can be evaluated from Eqn. (6): $\Delta\sigma = \sigma_{lLq}(K\cos\theta - 1)$. Since the microprofile of the rough surface suggests a value of $K \simeq 1.03$, we conclude that $\Delta\sigma \simeq 0.02\sigma_{Hg}$ (angle of contact $\theta \simeq 7°$). Taking[66] $\sigma_{Hg} = 470$ erg cm^{-2}, the final result is $\Delta\sigma = 10$ erg cm^{-2}.

The other quantities needed to compute the coefficients A_1 and A_2 were taken to be: $\eta = 0.016$ P, $\delta = 13.6$ g cm^{-3}, $\kappa = 9$, and $a = 1$ mm.

Inspection of Table 2 shows that experimental and calculated values differ by no more than a factor of 1.5–2. In view of the tentative nature of the calculations, agreement to the nearest order of magnitude can be considered satisfactory.

4. INFLUENCE OF VOLUME DIFFUSION ON THE SPREADING OF LIQUID METALS

In the present section we shall discuss the third stage of the process, which determines the final size of the mercury spot[74,75]. The results for the one-dimensional and the two-dimensional cases, shown in Fig. 6, indicate a power law of the form $X = B_1 m^{p_1}$ and $R = B_2 m^{p_2}$ respectively for the final distance X from the centre of the drop, to which a mass m of mercury will spread along a channel, and for the final radius R in the case of circular wetting.

Fig. 7 gives the times t_k, arbitrarily chosen as corresponding to completion of the process, by extrapolation of the second stage, *i.e.* by replacing the logarithmic rate plot by two straight lines, as in Fig. 8. It can be seen that the value of t_k is related to the mass of the sample by a power law: $t_{k(1)} = C_1 m^{q_1}$, $t_{k(2)} = C_2 m^{q_2}$ (for the one-dimensional and the two-dimensional case respectively).

For an approximate quantitative analysis of the experimental results, we consider two competing processes: the spreading of mercury on the zinc surface and its "sinking" into the specimen as a result of volume diffusion[75].

We shall deal first of all with the one-dimensional case, for which the equation of motion of the mercury front during the second stage can be written as $(x^2/m_1)dx = (\Sigma/\kappa)dt$ (see

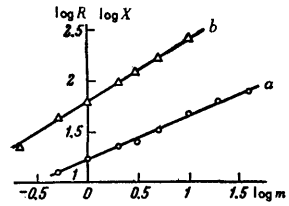

Fig. 6. (*a*) Variation of the final radius R (mm) of the mercury spot, and (*b*) variation of the final distance X (mm) to which mercury spreads by wetting a channel 1 mm wide, with the mass m (mg) of a mercury drop.

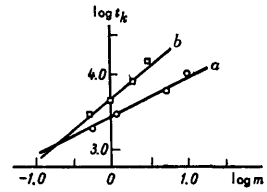

Fig. 7. Variation of the time t (seconds) of completion of wetting with the mass (m) of the drop (mg): *a*) for circular wetting; *b*) for wetting along a channel.

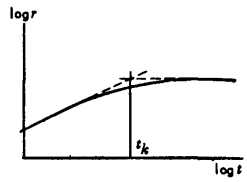

Fig. 8. Determination of the time of completion of wetting t_k (schematic).

Section 3). Allowing for volume diffusion, we must replace the quantity m_1 by the difference $m_1 - \Delta m_1(t)$, where Δm_1 is the mass of mercury absorbed by the specimen up to time t (per unit channel width and on one side of the initial location of the drop). The quantity Δm_1 can be evaluated as follows. Assuming to a first approximation that the volume diffusion coefficient D of mercury in zinc is independent of the concentration of mercury in solid solution, the weight of mercury (in grammes) which has gone into solution in the zinc at time $t(x)$ from the element $d\xi$ is $2c_0(D/\pi)^{1/2}[t(x) - t(\xi)]^{1/2}d\xi$, where $t(\xi)$ is the time at which the mercury front reaches position ξ, $t(x)$ the time at which the front reaches position x ($x > \xi$), and c_0 the concentration of mercury in the surface layer. Integrating with respect to $d\xi$ from 0 to x, we obtain

$$\Delta m_1 = \frac{2}{\sqrt{\pi}} c_0 \sqrt{D}\sqrt{t(x)}\, x S_1,$$

where $S_1 \lesssim 1$ is a dimensionless quantity determined by the form of the relationship $x = x(t)$.

We can now write the equation of motion of the mercury front in the form

$$\frac{x^2}{m_1 - \Delta m_1}dx = \frac{x^2}{m_1 - (2/\sqrt{\pi})S_1 c_0 \sqrt{D}\, x\sqrt{t}}dx = \frac{\Sigma}{\kappa}dt. \qquad (16)$$

If, in this case, $x_1 = A_1 t^{n_1}$, it follows that

$$S_1 = \int_0^x \sqrt{1 - \frac{t(\xi)}{t(x)}}\frac{d\xi}{x} = \int_0^1 \sqrt{1 - \psi^{1/n_1}}\,d\psi = S_1(n_1),$$

i.e. S_1 is a quantity which depends only on n_1.

In the case under discussion the end of the process is described by the condition $m_1 = \Delta m_1$‡. In order to calculate to a first approximation the final distance X, we assume that the characteristic law for the second stage, $x = (3m_1\Sigma/\kappa)^{1/3}t^{1/3}$, applies also to the third stage. Then the value of X is determined by the condition $m_1 \simeq 2c_0(D/\pi)^{1/2}S_1 X[t(X)]^{1/2}$, where $t(X) = X^3\kappa/3m_1\Sigma = t_{k(1)}$ (see Fig. 8). Hence

$$X = (3\pi/4)^{1/5}S_1^{-2/5}(c_0 D^{1/2})^{-2/5}(\Sigma/\kappa)^{1/5}m_1^{2/5} = B_1 m_1^{2/5}, \qquad (17)$$

$$t_{k(1)} = [(\pi/4)\ 3^{-2/5}]^{2/5}\ S^{-4/5}(c_0 D^{1/2})^{-4/5}(\Sigma/\kappa)^{-2/5}m_1^{4/5} = C_1 m_1^{4/5}, \qquad (18)$$

where $S_1 = S_1(1/3) \simeq 0.84$.

Similarly, we find for the two-dimensional case,

$$\frac{r^2}{m - \Delta m} = \frac{r^2}{m - 2\sqrt{\pi}S_2 c_0\sqrt{D}\, r^2\sqrt{t}}dr = \frac{3}{2\pi}\frac{\Sigma}{\kappa}dt;$$

if $r = A_2 t^{n_2}$, the dimensionless coefficient S_2 is given by

$$S_2 = \int_0^r \sqrt{1 - \frac{t(\rho)}{t(r)}} \times \frac{2\rho}{r}\frac{d\rho}{r} = \int_0^1 \sqrt{1 - \psi^{1/n_2}}\ 2\psi\ d\psi = S_2(n_2).$$

The final radius R and the time $t_{k(2)}$ are given approximately by

$$R = (3/2\pi^2)^{1/5}S_2^{-1/5}(c_0 D^{1/2})^{-1/5}(\Sigma/\kappa)^{1/5}m^{2/5} = B_2 m^{2/5}, \qquad (19)$$

$$t_{k(2)} = (1/24)^{1/5}S_2^{-1}(c_0 D^{1/2})^{-1}(\Sigma/\kappa)^{-1/5}m^{1/5} = C_2 m^{1/5}, \qquad (20)$$

where $S_2 = S_2(1/4) = \pi/4$.

The theoretical values of the exponents of m in Eqns. (17)–(20) are in satisfactory agreement with experiment (see Table 3).

TABLE 3.

	p_1	p_2	q_1	q_2
Theory	2/5	2/5	4/5	1/2
Experiment	0.59	0.40	0.85	0.47

We may also compare the coefficients B and C. As in Section 3, let $\Delta\sigma = 10$ erg cm^{-2}, $\eta = 0.016$ P, $\delta = 13.6$ g $\times$ $\times$ cm^{-3}, and $\kappa = 9$. We shall assume that $D \simeq 10^{-11}$ cm^2 $\times$ $\times$ s^{-1} and $c_0 \simeq 1$ g cm^{-3}. (This choice is somewhat arbitrary, since it involves an estimate of the solubility of mercury in the zinc lattice; however, we believe our estimate of the quantity $c_0 D^{1/2}$ to be of the correct order of magnitude.) Introducing these values into formulae (17)–(20), we find: $B_1 = X/m_1^{p_1} = 282$ cm (g/cm)$^{-3/5}$, $C_1 = t_{k(1)}/m_1 = 1430 \times 10^3$ s (g/cm)$^{-4/5}$, $B_2 = R/m^{p_2} = 24.5$ cm g$^{-3/8}$, $C_2 = t_{k(2)}/m^{q_2} = 36.2 \times 10^3$ s g$^{-1/2}$.

The comparison with experiment is shown in Table 4.

Thus, the experimental and the calculated values of the coefficients B_2 and C_2 for the two-dimensional case are in fairly good agreement, but for the case of wetting along a channel the experimental values are appreciably lower than those predicted by theory. This may be due to a slight creep of the mercury, by surface diffusion, below the lacquer which covers the surface of the specimen on either side of the channel. This effect, which could be significant after prolonged periods (*i.e.* during the third stage), would lower the values of X and $t_{k(1)}$. Some discrepancies may be caused by variations in the width of the channel along its length. Nevertheless, considering the approximations involved in the derivation of the equations, and also in the previously derived rate equations, we may conclude that satisfactory agreement as to order of magnitude has been obtained also in the one-dimensional case.

The experiments so far described were conducted at room temperature. Since the diffusion coefficient D is more sensitive to temperature changes than the other quantities which appear in expressions (17)–(20), the time required for completion of the process and the final radius of the spot would both be expected to decrease with increase in temperature: in other words, the third stage should set in earlier and be completed more rapidly. Experimental results fully confirming these expectations are shown in Fig. 9 (for the two-dimensional case). The coefficient A_2 for the second stage remained constant at all temperatures. From the relation $R = f(1/T)$, shown in Fig. 10, the activation energy U for the volume diffusion of mercury in zinc can be calculated. Since $R =$ $= \text{const}[D_0 \exp(-U/kNT)]^{1/8}$, we find $U = 2.3 \times 8kNd\ (1/T) \times$ $\times \log(R/d) = 9.5$ kcal g-atom^{-1} $= 0.41$ eV/atom, in satisfactory agreement with published data[60,76].

Some interesting results on the role of volume diffusion in the final stage of formation of the mercury spot were also obtained by the following experiments. If a new mercury droplet is added at the centre of the spot before

TABLE 4.

	$B_1 = X/m^{p_1}$	$B_2 = R/m^{p_2}$	$C_1 = t_{k(1)}/m^{q_1}$	$C_2 = t_{k(2)}/m^{q_2}$
For a = 1 mm				
Theory	117 mm mg$^{-2/5}$	18.4 mm mg$^{-3/8}$	20.7×10^3 s mg$^{-4/5}$	1.2×10^3 s mg$^{-1/2}$
Experiment	69	17	4.5×10^3	2.8×10^3

‡ Note that the equation $m_1 = \Delta m_1$ is not strictly obeyed. A very thin layer of mercury remains on the surface up to the time when the spot stops growing, but this was calculated and found to have no appreciable effect on the expressions $X = X(m)$ and $R = R(m)$.

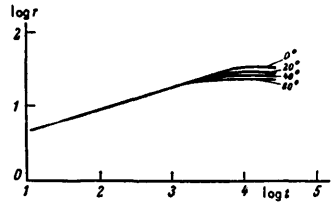

Fig. 9. Variation of the radius of a mercury spot r (mm) with time t (seconds) at different temperatures; drop mass m = 5 mg.

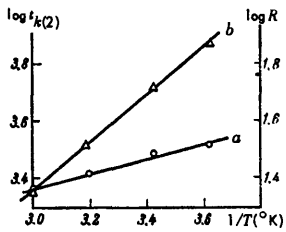

Fig. 10. *a*) Temperature variation of the final radius R (mm) of a mercury spot; *b*) temperature variation of the time $t_{k(2)}$ (seconds) of completion of the process; drop mass m = 5 mg.

completion of the main, second stage (*i. e.* before the process begins to slow down appreciably), its effect is found to be "additive", and the spot grows to approximately the same final size as would have been obtained if the whole mass of mercury had been added initially. However, if the second drop is added after 2–3 h, when the third stage has gone to completion, its effect is no longer additive: if the second drop is equal to the first, it has practically no effect on the size of the spot, if it is larger, the final radius corresponds to the spreading of the larger drop alone. At higher temperatures, the critical time interval (after which additivity ceases) decreases from several hours at room temperature to 3–5 min at 200°.

The importance of the volume diffusion (absorption) of mercury during the spreading of this metal on a zinc surface was also confirmed by mechanical experiments. If the plate is bent immediately after the experiment, the area which was originally covered with the mercury spot develops a network of fine cracks: this is an instance of embrittlement brought about by adsorption[17]. However, if the specimen is subjected to flexure after some time, no surface cracking is observed, which suggests that practically the whole of the mercury originally present on the surface has had time to diffuse into the bulk of the zinc. The critical storage time t_s, after which the embrittlement no longer occurs, decreases rapidly with increase in temperature:

Temperature, °C	20	50	100	150	200
t_s	3 days	3 h	45 min	12 min	5 min

5. DIFFUSION OF MERCURY AND GALLIUM ALONG A ZINC SURFACE

This section deals with some aspects of a more commonly observed type of spreading of liquid metals: surface diffusion.

The surface diffusion of mercury has been studied, mainly at room temperature, on polycrystalline zinc specimens. To remove oxide films, the specimens were immersed in a 10% solution of ammonia and kept in that solution throughout the experiment. This treatment produces a smooth surface (see Fig. 2*a*).

The main series of experiments was performed on square, horizontal plates, 0.8 or 1.85 mm thick. A small droplet of mercury was deposited at the centre of the plate, giving an angle of contact of ~ 7°. A matt, circular spot soon began to spread outwards from the drop. The radius of the spot was found to increase with time according to the equation $r = At^{0.5}$, the proportionality coefficient A being independent of the mass m of the original drop (Fig. 11). After several hours the drop disappears from the centre of the spot, the growth of the spot begins to depart from the law $r = At^{0.5}$, and eventually stops altogether. The final spot radius R is related to the intial mass m of the drop by the expression $R = Bm^p$, in which the exponent p had the value 0.35 in every experiment (Fig. 12)§.

Both the rate of growth and the final size of the matt spot increase with the mean grain size of the zinc. Thus, A = 0.2 and B = 20 for a grain diameter of 50 μm, whilst A = 0.12 and B = 12 for a grain diameter of 15 μm (r and R are in millimetres, t in seconds, and m in milligrammes).

Experiments with inclined, narrow zinc plates, 20 cm long and supported with their lower end in contact with a large (several grammes) mass of mercury, give convincing proof that the spreading of mercury on a smooth zinc surface involves a diffusion mechanism. When contact with the mercury had been established, a dull spot began to

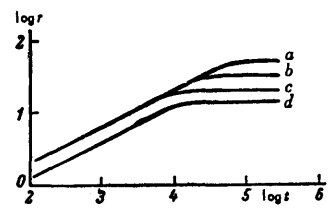

Fig. 11. Variation of the radius r (mm) of a mercury diffusion spot with time t (seconds) for mercury drops of different mass m on polycrystalline zinc of mean grain size 50 μm: *a*) 10 mg; *b*) 3 mg; *c*) 1 mg; *d*) ditto, on zinc of 15 μm mean grain size with mass m = = 1 mg.

§ Tracer experiments with radioactive ^{203}Hg confirmed that, as in the case of wetting, there was no appreciable difference at any time during the experiment between the visual and the autoradiographic methods of detecting the leading edge of the spot.

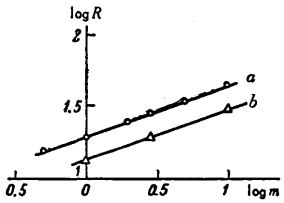

Fig. 12. Variation of the final radius R (mm) of a mercury diffusion spot with mass m (mg) of the mercury drop for zinc specimens of different mean grain size (μm): *a*) 50; *b*) 15.

spread upwards along the surface of the plate. It was found (Fig. 13) that the motion of the leading edge of the spot follows the law $h = At^{0.5}$, and that the coefficient A has the constant value $A = 0.2$ mm $s^{-1/2}$ irrespective of the inclination of the plate to the horizontal (from 10° to 90°). Thus, the rate at which the mercury spreads is not affected by gravity forces, and this must mean that the process occurs by diffusion (see Section 3).

The observed relationship between the radius of the dull spot and time agrees well with the expressions which describe two-dimensional diffusion in an infinite plane from a point source of mass m. It is known[18] that

$$c_0 = (m/4\pi D_s t)\exp(-r^2/4D_s t),$$

(D_s is the surface diffusion coefficient, c_0 is the concentration of diffusing material at a point in the plane at distance r from the source). It follows that

$$r = 2D_s^{1/4}[\ln(m/4\pi D_s c_0 t)]^{1/4} t^{1/4}. \qquad (21)$$

The logarithmic term varies relatively slowly for a fairly long time, and can therefore be ignored to a first approximation. Thus, Eqn. (21) can be replaced by the expression $r = \text{const} \times t^{1/2}$, which is in complete agreement with the experimentally observed variation of r with t during the main stage of the spreading process. Departures from the law $r = At^{1/2}$ occur only some considerable time after the beginning of the experiment, when the decrease in the logarithmic term becomes appreciable.

The problem of diffusional spreading of atoms from a melt on the free solid surface of a metal in which the liquid metal is soluble to some extent is analogous to the problem of grain boundary diffusion with allowance for volume diffusion. This problem has been discussed by

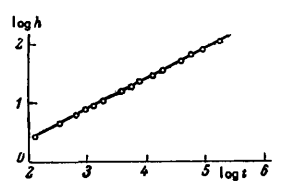

Fig. 13. Variation of the height h (mm) of the edge of the spot with time t (seconds) for diffusional spreading of mercury on inclined zinc plates with a smooth surface.

Fischer[77], Whipple[78], and McLean[79], who studied the concentration of diffusing material as a function of time and of depth of penetration.

In our present system we shall apply the concepts previously developed[75] to describe the spreading of a liquid mercury phase to a semiquantitative evaluation of the dependence of the final radius of the mercury spot upon the mass of the mercury drop. The model compares the sideways spreading of mercury along the surface from the central drop with the bulk diffusion of mercury into the specimen through the surface of the spot.

To apply this model, we consider an annular element of width $d\rho$ at a distance ρ from the original location of the drop. The leading front of the spot will reach this element at time $t(\rho) = (\rho/A)^2$. It is assumed that the penetration of mercury into the specimen can be described by the conventional volume diffusion equation with a constant diffusion coefficient D. Then, if dm is the weight (in grammes) of mercury which passes into the bulk from the annulus up to the time (t_k) when the spot ceases to grow, we can write[20¶]

$$dm = (2/\pi^{1/2})\, c_0 \{D[t_k - t(\rho)]\}^{1/2} 2\pi\rho\, d\rho.$$

Equating the total amount of mercury diffusing into the bulk from the entire surface of the spot to the mass m of the original drop, we have

$$m = 4\pi^{1/2}(c_0 D^{1/2}) \int_0^R [t_k - t(\rho)]^{1/2} \rho\, d\rho,$$

whence we obtain the final equation

$$R = (3/4\pi^{1/2})^{1/3} A^{1/3} (c_0 D^{1/2})^{-1/3} m^{1/3} = Bm^{1/3}. \qquad (22)$$

Thus, the calculated exponent of the mass m of the drop is 1/3, which agrees very closely with the experimental value of 0.35.

It is interesting to compare the experimental and the calculated values of the coefficient B in Eqn. (22). We shall assume that $D = 10^{-11}$ cm^2 s^{-1}, and $c_0 = 1$ g cm^{-3}.

From the data of Fig. 11, we take the value $A = 0.02$ cm $s^{-1/2}$. Introducing this into Eqn. (22), we obtain $B = 14$ cm $g^{-1/3}$, in good agreement with the experimental value ($B = 20$).

Allowance for the volume diffusion of mercury can also explain the influence of grain size on the rate of growth of the mercury spot and on its final size. Clearly, mercury can accumulate faster in the surface layer, the more slowly it is removed from the surface into the bulk of the specimen. Since diffusion along grain boundaries is much faster than diffusion within the grains[77-79], fine-grained material can "absorb" the mercury more readily than coarse-grained material, and this retards the spreading of the visible matt front. For the same reason, the final spot size is less on microcrystalline than on coarsely crystalline zinc.

The fundamental role played by volume diffusion in arresting the growth of the diffusion spot on the surface is very clearly brought out by data on the effect of temperature. Both processes involved in the growth of a dull

¶ The assumption of a constant concentration c_0 over the whole of the spot is quite correct in the case of a liquid film spreading over a metal surface, but it is not strictly applicable to the problem of diffusional spreading. However, for the purpose of the present semiquantitative calculation, the assumption does not materially affect the final result.

spot around a mercury drop, surface diffusion and volume diffusion, are strongly temperature-dependent. But since the activation energy for volume diffusion is significantly higher than for surface diffusion[52], one would naturally expect the absorption of mercury into the bulk to be more strongly affected by temperature changes than the surface spreading. In other words, an increase in temperature should increase the rate of growth of the spot, and decrease its final dimensions. This conclusion, deduced from the proposed mechanism for the growth of the spot, was fully confirmed by experimental results (Fig. 14) obtained between 0° and 80°.

These data also enable us to evaluate the activation energy U_s attending the surface diffusion of mercury on zinc. Since the rate of growth of the spot is described with sufficient accuracy, in the experimental temperature interval, by the equation $r = A^* t^{1/2}$, where A^* is a function of temperature, we can introduce $A^* = QD_s^{1/2}$, where Q is a constant. If we also assume that the equation for the effect of temperature on the surface diffusion coefficient has the usual form $D_s = D_{s0} \exp[-U_s/kNT]$, we can readily show that

$$U_s = -2.3 \times 2kN[d \log A^*/d(1/T)].$$

The experimental value of $[d \log A^*/d(1/T)]$ from Fig. 15 leads to $U_s = 5.5$ kcal mole^{-1}.

The spreading of gallium on zinc has been studied mainly at 35°, *i.e.* a few degrees above the melting point of gallium (29.7°). The medium used to dissolve the oxide film on zinc was, as before, a 10% solution of ammonia. The sample of gallium was melted before being deposited on the specimen surface.

On a smooth zinc surface, gallium forms a drop with an angle of contact of ~ 60°; a rather indistinct spot with a diffuse leading boundary† grows around the drop according to the law $r = A_g t^{0.5}$ (Fig. 16).

Unlike mercury, gallium cannot wet even a rough zinc surface. This is because gallium, in order to wet the surface, needs microdepressions and grooves having a vertex angle not greater than 60°; the microprofile traces of Fig. 2*b* show that defects of this type are almost completely absent even on the roughest surface.

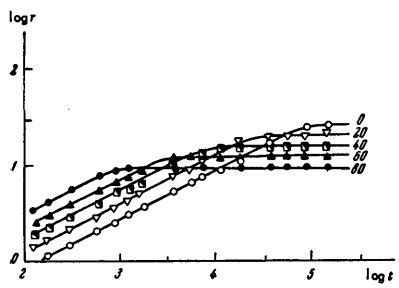

Fig. 14. Variation of the radius r (mm) of a mercury diffusion spot with time t (seconds) for different temperatures. Mass of drop m = 3 mg.

† As in the study of the surface diffusion of mercury, the measurements were checked by using the radioactive isotope ^{72}Ga. The autoradiographic results were in good agreement with visual observations of the growth of the spot.

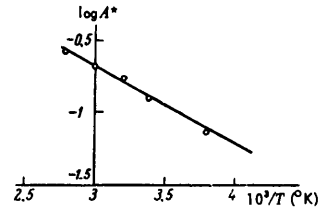

Fig. 15. Variation of the parameter $A^* = \text{const} \sqrt{D_S}$ with temperature.

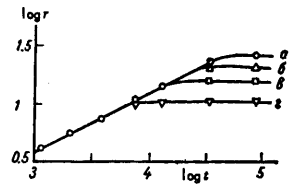

Fig. 16. Variation of the radius r (mm) of a gallium spot with time t (seconds) for drops of different mass m (mg): *a*) 100; *b*) 50; *c*) 30; *d*) 5.

The rate of growth of the gallium spot is lower than that of the mercury spot by about a factor of two: $A_g = 0.13$ mm × × s$^{-1/2}$ for a grain diameter of 50 μm.

The mean radius of the gallium spot is related to the mass of the drop by the expression $R = B_g m^{p_g}$ (Fig. 17), where $p_g = 0.30$. This agrees satisfactorily with the theoretical equation (22).

One characteristic difference between the spreading of gallium and that of mercury is grain boundary diffusion, which is more pronounced in the case of gallium. Thus, if a gallium drop is placed on the surface of a zinc plate 0.8 mm thick, a dull spot begins to grow on the opposite surface shortly afterwards, with its centre immediately below the original site of the drop.

The importance of intergranular diffusion in the spreading of gallium on zinc was confirmed by mechanical testing of the specimens. If the zinc plate is bent after the gallium spot has stopped growing, surface microcracks appear not only within the spot, but also several millimetres ahead of its boundary. (Zinc plates on which mercury has been

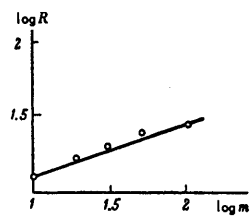

Fig. 17. Variation of the final radius R (mm) of a gallium spot with the mass m (mg) of the drop.

allowed to spread develop a roughness, when bent, which is strictly confined to the area of the spot.)

The pronounced grain boundary diffusion increases the rate at which gallium is absorbed into the bulk. As a result, the final spot diameters are relatively small (B_g = = 4.7 when R is in millimetres and m in milligrammes, as compared with B = 20 for the spreading of mercury). Using Eqn. (22), it can be shown that the volume diffusion coefficient of gallium in zinc is 10^{-8}–10^{-9} cm s^{-1}, *i.e.* by two or three orders of magnitude higher than that of mercury. Since the solubility of gallium in zinc is lower than that of mercury, such a large diffusion coefficient can only be explained by invoking fast diffusion along the grain boundaries.

An analysis of the spreading of liquid metals on solid metallic surfaces shows that the major factors which influence the process are: the relative magnitudes of the surface energy of the solid metal, the liquid metal, and the interfacial boundary; the microprofile of the solid surface; the nature of the medium to which the contacting metals are exposed, its temperature, the state of the surface of the solid metal (presence of oxide films, etc.), and the structure of the layer just below the surface; the solubility of the liquid metal in the solid metal and the rate of volume diffusion of atoms from the melt into the solid metal; the physical properties of the liquid (density, viscosity, etc.); the activation energy for surface diffusion; and some other factors (*e.g.* the possibility of formation of intermetallic compounds).

Quantitative relationships describing the spreading of a melt on a solid surface have been derived without making any special assumptions as to the nature of the contacting metals, except for assuming a low solubility of the melt in the solid phase and the absence of chemical interactions between the components‡.

The new ideas on the surface spreading of liquid metals, and the quantitative relationships which have been derived from them, can be applied to various physicochemical problems involving interaction between liquid and solid metals. This is particularly true of the development of macroscopic failure cracks in the presence of melts showing high adsorption activity[81,82], of soldering and welding, of the deposition of protective metallic coatings, and of many types of spreading of a liquid phase or of an adsorbed layer in porous bodies (for example, in catalysts), and so on. The observations reported are also relevant to the behaviour of liquids on solid surfaces under conditions of weightlessness[83].

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‡ According to the phase diagram for binary Zn–Hg melts, there are no chemical interactions between the components, and the formation of intermediate phases is very doubtful. For the Zn–Ga pair, the phase diagram shows complete absence of chemical interactions[80].

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METHODS OF PREPARATION OF SEMICONDUCTING COMPOUNDS

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1. INTRODUCTION

Among the semiconducting materials used in present-day electronics and radio technology, a number of chemical compounds covering a wide range of physical properties in different combinations occupy an important place. These are finding increasing application in modern technology, and their number is growing.

In many cases, great difficulty has been encountered in developing methods of preparation of compounds with semiconductor properties. Whereas the well-established techniques of silicon and germanium production could be applied directly to some of these materials, many semiconducting compounds have needed far more complex apparatus and production techniques because of the high reactivity of the compounds themselves (and of their constituent elements), and because of the high melting points and dissociation pressures involved. However, many different preparation techniques, highly relevant to semiconductor technology, have already been established (synthesis, purification, doping, and single-crystal growth).

Apart from a number of unrelated communications, describing individual apparatus and production techniques, the technical literature contains very few critical reviews of our fund of experimental knowledge. Folberth[1] has published a fairly comprehensive survey of the methods of preparation of semiconducting compounds of the $A^{III}B^{V}$ group, including a physicochemical discussion of the nature of these compounds. The methods of preparation of various compounds are dealt with, to some extent, in a number of monographs[2-6] and proceedings of conferences[7-14]. Goryunova[15] and Borshchevskii[16] have reviewed the methods of preparation and the properties of compounds which exhibit semiconductor properties. There are also two bibliographic reviews, edited by Zhuze[17,18].

2. CLASSIFICATION OF THE METHODS OF PREPARATION OF SEMICONDUCTING COMPOUNDS

Folberth[1] proposed that the method of preparation of semiconducting compounds should be classified in accordance with the physicochemical properties of the compounds themselves: (1) compounds whose vapour pressure is negligible at the melting point (antimonides); (2) compounds having a significant vapour pressure at their melting point (arsenides and phosphides of indium and gallium); (3) compounds with high melting points and high vapour pressures over the melt (aluminium arsenide and phosphide, nitrides, borides).

Hilsum and Rose-Innes[2] have divided the basic methods of preparation of semiconducting compounds (of the $A^{III}B^{V}$ type only) into four groups: (1) crystallisation from stoichiometric melts (gallium and indium antimonides and arsenides); (2) crystallisation from non-stoichiometric melts (phosphides); (3) condensation from the vapour phase (indium and gallium arsenide and phosphide), including iodide methods; (4) chemical reactions (aluminium, boron, and gallium phosphides and nitrides).

This subdivision of techniques is valuable from the point of view of technology, because the methods of the first two groups enable the compounds to be produced in single-crystal or coarsely crystalline form, whereas the third and fourth groups lead to fine needlelike and platelet crystals, and to films[2]. Hilsum and Rose-Innes' classification[2] is more rational than Folberth's[1].

In the present article, we shall consider the known methods of preparation of semiconducting compounds under two headings: direct and indirect. The criterion for this classification is the chemical nature of the substances used as starting materials, irrespectively of their state of aggregation.

The direct methods are those in which the starting materials are components of the compound being synthesised. Since these methods are closely concerned with crystallisation — the production of compounds in a single-crystal or coarsely polycrystalline form — they had already reached a high stage of development in connection with technologically simpler compounds, and gave satisfactory results with relatively minor modifications.

The direct methods of preparation of semiconducting compounds consist, as a rule, in bringing together the starting components and removing the reaction product from the reaction zone by converting it into a different state of aggregation. The synthesis can be carried out either continuously or batch-wise. The initial mixture of starting components can be gaseous, liquid, or solid, or it can be a mixture of phases in different states of aggregation. The compound must be produced in the solid state, however, and therefore the most important processes are crystallisation from solution, from the melt, and from the vapour phase, since these lead to crystalline products.

It may be impossible to bring the starting components into direct contact: in this case a carrier must be used. The simplest carrier is a neutral gas.

Thus, the direct methods can be subdivided according to the nature of the process leading to the formation of the crystalline compound (crystallisation; condensation with formation of a solid or liquid compound, followed by crystallisation if the compound is obtained in the liquid form; sintering, which is based on the diffusional transport of the components; etc.).

However, if even a single participant of the reaction is a chemical compound able to react with the other components or constituents of the starting mixture, the method of synthesis should be termed "indirect". Methods of this type are often referred to as "chemical methods" in the literature[2]. In most cases the compounds are produced in a crystalline form, but finely divided.

According to the type of reaction employed, indirect methods can be subdivided into two groups: (1) methods relying on double decomposition reactions, and (2) methods relying on thermal decomposition reactions. Reactions of both types may also occur together.

The reactions can take place in a homogeneous or a heterogeneous medium. This has a profound effect on the design of suitable apparatus; the classification of synthetic methods should therefore include this aspect.

Methods of synthesis relying on reactions in a homogeneous phase can be divided into gas-phase (or vapour-phase) methods, and methods of preparing compounds from condensed phases.

In the gas (or vapour) phase, compounds can be synthesised in a stream of carrier gas or in a stream of one of the reactants.

Indirect methods are often used as preliminary synthetic operations, followed by conversion of the resulting compounds into compact specimens, or single crystals, by one of the direct methods. We therefore propose to discuss first the indirect methods, and then the direct methods of preparing compounds.

The indirect methods usually afford crystalline compounds in a highly disperse form. Nevertheless, they have been widely applied in the synthesis of high-melting, decomposable compounds having high dissociation pressures and high chemical reactivity.

The classification of methods for the preparation of semiconducting compounds presented here is, undoubtedly, neither definitive nor complete. Other grounds on which to base a classification could probably be suggested. However, it has enabled us to assign to well-defined classes all published preparative methods of which we were aware, and to arrange the present review within the framework of an explicitly stated classification.

3. INDIRECT METHODS OF PREPARATION OF SEMICONDUCTING COMPOUNDS

Reactions in the Condensed Phase

Reactions in the condensed phase are used comparatively seldom.

Montignie[19] prepared aluminium phosphide by heating a mixture of red phosphorus, aluminium oxide, and potassium cyanide in a closed crucible. The product, which was a mixture of aluminium phosphide and phosphate, was treated with hydrochloric acid, which dissolved the phosphate (and some of the phosphide). The insoluble residue, heated to 600°, was found to be aluminium phosphide of stoichiometric composition.

Effer and Antell[20,21] prepared the phosphides and arsenides of indium and gallium by oxidation–reduction reactions between a chloride of the metal and the metalloid:

$$3GaCl_2 + As \rightarrow 2GaCl_3 + GaAs$$

or

$$2InCl + P \rightarrow InCl_2 + InP,$$

or between a chloride of the metalloid and the metal:

$$AsCl_3 + 2In \rightarrow InCl_3 + InAs.$$

To prepare gallium arsenide, liquid gallium dichloride was heated at 500° for 24 h with powdered arsenic in a nitrogen atmosphere. The resulting gallium arsenide was mechanically separated from the small amount of gallium formed by the reaction, and heated *in vacuo* at 600°.

Metal phosphides have been prepared by the reaction between liquid white phosphorus and indium monochloride (or gallium dichloride) at 300° in a nitrogen atmosphere for 1 h. The complex compounds produced by the reaction were decomposed by heating the mixture to 500°, giving indium or gallium phosphide.

Arsenic trichloride and indium, in stoichiometric proportions, were heated to 350° in evacuated and sealed bulbs. The free end of the bulb was then moved out of the furnace, and the end containing the reaction product was heated to 600°. This caused the volatile materials which had escaped reaction to condense on the cold end of the bulb. The yield of arsenides was in excess of 95%; that of phosphides ~ 65%.

Addamiano[22] used a different type of reaction in the condensed phase to prepare phosphides:

$$2M + Zn_3P_2 \rightarrow 2MP + 3Zn,$$

where M = Al, Ga, or In. The reaction was carried out in a stream of argon in order to carry away the zinc vapour and to protect the reactants from oxidation. Aluminium phosphide was synthesised at 1000–1100° in the course of 30 min, gallium phosphide at 800° in 12–24 h, and indium phosphide at 700–800° in 24–48 h. The yield of final product was very small in the last reaction.

Reactions in the Vapour Phase

Reactions in the vapour phase have been widely used in the preparation of a great variety of semiconducting compounds.

Frerichs[23] grew crystals of cadmium sulphide by the reaction between cadmium vapour and hydrogen sulphide in a stream of hydrogen. The cadmium was placed in a boat heated to 800–1000°. The hydrogen sulphide was introduced into the reaction close to the boat, where it became mixed with the cadmium vapour. The cadmium sulphide produced was deposited on the walls of the reactor as crystalline platelets 20 × 30 × 0.22 mm in dimensions. Cadmium selenide and telluride crystals can also be grown by this method.

Gershenzon and Mikulyak[24] synthesised gallium phosphide crystals by a different method, based on the reaction between vapours of phosphorus and gallium monoxide in a closed volume. Gallium monoxide vapour was generated by the reaction

$$Ga_2O_3 + 4Ga \rightarrow 3Ga_2O.$$

A quartz dish containing a mixture of gallium trioxide and gallium in 1 : 4 molecular proportions was placed at the upper end of an evacuated and sealed quartz bulb. The lower end of the bulb contained red phosphorus. The bulb was inserted vertically into a furnace designed to keep the upper end of the bulb at 975–1060°, and the lower end at 350–400°. The two regions of controlled temperature were joined by a smooth temperature gradient. The gallium monoxide vapour migrates towards the cooler end of the bulb, where it reacts with the phosphorus vapour:

$$5Ga_2O + 3P_4 \rightarrow 10GaP + P_2O_5.$$

This reaction produces needlelike crystals of gallium phosphide, 1–20 mm long, on the walls of the bulb. In some cases the reaction is carried out in a stream of inert gas. Effer and Antell[21] prepared gallium arsenide by passing gallium dichloride and arsenic vapour, in a stream of pure nitrogen, through a heated quartz tube. The vapours were led to a mixer from separately heated generating flasks. The gas mixture in a stream of carrier gas was introduced into a quartz tube at 800°, and thence into another tube at 600° where gallium arsenide crystals were deposited as a fine powder and separated from the unreacted volatile materials. A yield of final product as high as 75% was obtained in one experiment.

Reactions in Heterogeneous Media

Reactions in heterogeneous media, like those in the vapour phase, have been widely used to synthesise various types of semiconducting compound.

A good example is the method of preparation of gallium phosphide developed by Samsonov *et al.*[25], who reduced gallium trioxide with phosphine:

$$Ga_2O_3 + 2PH_3 \rightarrow 2GaP + 3H_2O.$$

The reaction was carried out in a tube furnace at 950° for several hours. The phosphine was generated by decomposing aluminium phosphide with water. A similar process was proposed by Lewis[26], who reduced gallium trioxide with phosphorus vapour at 1000° in a stream of argon or argon–hydrogen mixture. The resulting gallium phosphide powder (particle size 1 μm) was densified by recrystallisation at 1050° for several hours.

Semiconducting compounds can be used as starting materials. Thus, Addamiano[27] synthesised aluminium nitride by nitriding aluminium phosphide with ammonia:

$$AlP + NH_3 \rightarrow AlN + \tfrac{1}{4}P_4 + \tfrac{3}{2}H_2.$$

Powdered aluminium phosphide was heated at 1000–1100° in a stream of ammonia for 1–2 h. Gallium nitride was prepared by the same method and under the same conditions by using gallium phosphide or arsenide in place of aluminium phosphide.

Although organometallic compounds should, in principle, lead to purer synthetic materials, their use in the preparation of semiconducting compounds has been rather limited. A patent application by Didchenko[28], claiming the preparation of indium phosphide by the reaction between an organometallic compound of indium and phosphorus in a hydrogen stream at 300°, is one of the few publications dealing with this problem. By working at lower temperatures, it should of course be possible to minimise by this method the contamination of the final product arising from interactions with the apparatus and with the atmosphere.

Another example of the use of heterogeneous reactions in the synthesis of semiconducting compounds is Tsymbalov and Trushina's low-temperature synthesis[29] of gallium selenide by passing gaseous hydrogen selenide through a solution of gallium trichloride at pH 6.5–7 and at a temperature of ~80°.

Mill' and Naumova[30] prepared ferrite crystals ($Y_3Fe_5O_{12}$) with a garnet structure from aqueous solutions containing Y_2O and Fe_2O_3 in proportions between 3 : 1 and 1 : 10. The reaction was carried out under autoclave conditions (1500 atm, 500°) during 5–15 days. The resulting equiaxial crystals had dimension of ~1.5 mm.

Thermal Decomposition Reactions

Methods of preparation of semiconducting compounds based on the thermal decomposition of more complex starting materials are relatively seldom used. A typical example is Renner's procedure[31] for the preparation of aluminium, gallium, and indium nitrides by decomposition of their monoammines in the vapour form ($MCl_3.NH_3$, where M = Al, In, or Ga) on a hot substrate. A graphite disc, which can be heated by a high-frequency induction heater, is placed in a quartz bulb within a quartz tube. The monoammine of the desired metal is heated in a separate electrical resistance furnace. The preparation conditions requiring control include the temperatures of the substrate and of the monoammine, and the pressure in the bulb. The perfection of the crystals deposited on the substrate can be improved by rotating the graphite disc. Substrate temperatures were controlled (with rotation of the crystals) at 1000–1400° for AlN, ~1000° for GaN, and 600° for InN.

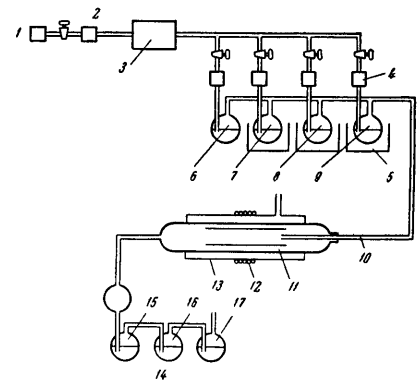

Fig.1. Apparatus for preparing silicon carbide single crystals by thermal decomposition of a gas mixture:
1) hydrogen supply; 2) pressure reducing valve;
3) gas purifier; 4) flow meter; 5) thermostats;
6) mineral oil; 7) silicon tetrachloride; 8) toluene;
9) compound of the doping element;
10) inlet for gas mixture; 11) graphite tube;
12) high-frequency induction coil;
13) water-cooled jacket; 14) scrubbers for side-products;
15) mineral oil; 16) methanol; 17) alkali solution.

To prepare crystalline silicon carbide, Ellis[32] decomposed a mixture of gases which he introduced, in a hydrogen stream, into a quartz reactor containing a graphite cylinder heated by an external high-frequency set (Fig. 1). The silicon-containing gas was silicon tetrachloride or trichlorosilane vapour; the carbonaceous gas was toluene, methane, carbon tetrachloride, or chloroform. The single crystals obtained had a diameter of 4–5 mm.

4. DIRECT METHODS OF PREPARATION OF SEMICONDUCTING COMPOUNDS

Condensation

Condensation is used in the direct synthesis of compounds from their components.

Bishop and Liebson[33] prepared crystals of cadmium sulphide by the following method. Metallic cadmium was heated to 650°, and sulphur to a temperature above 400°. The reaction chamber had a temperature of 1000°. The vapours of the components were transported to the reaction chamber by separate gas streams of argon–hydrogen mixture. CdS crystals condensed on the walls of the reactor as platelets a few square centimetres in area and up to 1 mm thick.

Scharowsky[34] prepared zinc oxide crystals in an apparatus in which the zinc was heated to 600° in a stream of nitrogen containing 1% of hydrogen. This carried the

zinc vapour to a reactor at 1150° connected to atmosphere. ZnO crystals grew on the walls in the form of needles up to several centimetres in length and 0.2 mm thick.

Sintering

Semiconducting compounds have been prepared by sintering [35,36].

Goryunova and coworkers [35] obtained small crystals of indium phosphide of stoichiometric composition by heating a compact of indium and phosphorus powders. The excess of phosphorus was distilled off by heating *in vacuo*. Watson [36] prepared cadmium and zinc sulphides, selenides, and tellurides by gradually heating the powdered elements to 450° at a rate of 0.5 deg min^{-1} in a vacuum.

Resublimation

Sublimation has been frequently used in the preparation of infusible semiconducting compounds [37-39].

Reynolds and Czyzak [37] grew single crystals of zinc sulphide from powdered zinc sulphide in a sealed quartz bulb filled with hydrogen sulphide at 0.42 atm pressure. The bulb was heated to 1250° for 2–4 days, with a smooth temperature gradient along its length. The single crystals obtained by this method had dimensions of 2 × 2 × 10 mm. Crystals of cadmium sulphide were prepared by a similar technique [38].

Cadmium sulphide has been resublimed in a stream of inert gas (helium) [39]. The compound was doped, during the sublimation, with a component placed in a separately heated zone. A temperature gradient of 10–40 deg mm^{-1} was established along the length of the furnace. The crystals were obtained as a condensate on a water-cooled tube, and had needlelike and platelet habits.

The resublimation method is the main method of preparation of silicon carbide crystals at present [40-44]. Lely [40] was among the first to use it. The raw, granular silicon carbide was loaded into a container between two coaxial graphite cylinders. The inner cylinder had a number of orifices through which the silicon carbide vapour could penetrate to the cooler central region. The cylinder was heated in a furnace to 2500–2600° for 6–8 h. The process was carried out in a hydrogen, argon, or carbon monoxide atmosphere. A radial temperature gradient, from the outer to the inner cylinder, was maintained in the furnace: crystal growth occurred along this gradient. The crystals obtained were ~ 10 mm long and 2–3 mm thick. The silicon carbide crystals were doped by introducing volatile phosphorus, aluminium, or boron compounds into the furnace atmosphere.

The method was later used with minor modifications [41,42], such as operation in a vacuum or under pressure, the use of seeds, and of different kinds of container, etc.

Some very recently developed resublimation methods form a special group of procedures for the preparation of compounds by condensation from the vapour phase.

These processes occur *via* the dissociation of the compound. The components interact with the vapour of a "third" component, forming volatile compounds, in the hotter regions. The volatile compounds diffuse to the cooler regions, where they dissociate to give products capable of interacting to re-form the desired compound. Reactions of this type have been termed "transport" reactions [43].

Transport reactions are most commonly used for growing epitaxial layers of semiconducting compounds on oriented single-crystal substrates of germanium, silicon, or other semiconductors. The deposits can be doped to the desired conductivity type and physical properties by introducing into the reaction tube small amounts of zinc, cadmium, magnesium, aluminium, or other metal chlorides. Different types of $p-n$ junctions can be produced [44] by depositing a compound of one conductivity type on a substrate of the opposite conductivity type.

Antell [45] prepared large crystals of gallium phosphide by resublimation in the presence of iodine vapour in the apparatus shown schematically in Fig. 2. Resublimation proceeds by the reactions

$$3GaP + 3I \rightarrow 3GaI + 3P,$$
$$3GaI + 2P \rightarrow GaI_3 + 2GaP.$$

The starting crystals were maintained at a temperature of ~ 1000°. New crystals grew on the walls where the temperature was ~ 800°. The concentration of iodine vapour in the bulb was ~ 1.2 mg cm^{-3}. Gallium phosphide crystals were prepared [46] by a similar method, using hydrogen as the transporting agent. Ikada and Kano [47] prepared gallium arsenide by this method, using single-crystal germanium as a seed. In contrast to previous workers, Newman and Goldsmith [48] prepared gallium arsenide crystals in a stream of hydrogen and hydrogen chloride rather than in sealed ampoules.

Crystallisation

The most widely used methods of preparation of compounds rely on the process of crystallisation. This large group of methods can be further subdivided according to the mode of crystallisation involved: normal freezing; normal directional freezing (the Bridgman–Stockbarger method); pulling from the melt (the Czochralski–Kyropoulos method); zone melting (Pfann's method); the Verneuil method; etc. The methods of fractional crystallisation shown diagrammatically in Fig. 3 are very useful technologically for compounds which decompose. The Verneuil method is similar in principle to zone recrystallisation, but it has not been used in its original form for the preparation of semiconducting compounds.

Fractional crystallisation from the melt to give a compounds shows some features which depend on whether the

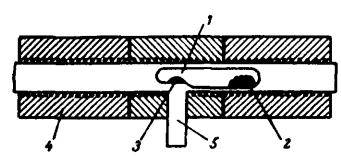

Fig. 2. Apparatus for preparing single crystals of gallium phosphide or gallium arsenide by resublimation in iodine vapour:
1) quartz ampoule filled with iodine vapour; 2) crystalline charge of the desired compound; 3) growing crystal; 4) three-zone furnace; 5) side-tube with inspection window.

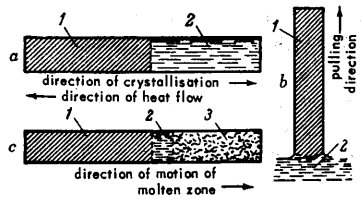

Fig.3. Basic fractional crystallisation methods:
a) normal directional freezing;
b) pulling from the melt (produces specimens of variable composition);
c) zone recrystallisation;
1) crystallised section; 2) melt; 3) solid charge.

process is carried out horizontally or vertically. The vertical variants of the zone recrystallisation technique can be operated without a container†.

In the vertical variants, account must be taken of gravity effects on the upward and downward diffusion of the components. Little use has been made as yet of intermediate (inclined) variants.

These methods of crystallisation were originally developed for compounds which do not decompose [49-83].

The work of Usachev *et al.* [49] on the synthesis of mercury selenide and telluride in thick-walled quartz bulbs is an example of the preparation of compounds by normal (free) crystallisation. A mixture of mercury and powdered selenium or tellurium was heated to 800° or 675° respectively over a period of 6–8 h, kept at this temperature for 20–30 min, and slowly allowed to cool. Kolomoets and Popova [50] prepared aluminium antimonide by melting the components in an alundum crucible within an evacuated quartz bulb. After the synthesis had taken place at 1200°, the bulb was inverted and the melt was cast into a hollow stopper made of graphite. Normal crystallisation was then allowed to proceed in this graphite crucible.

Often, compounds are prepared by direct fusion of the components, with normal crystallisation from the melt, followed by subsequent directional crystallisation.

The method of normal directional freezing for the preparation of compounds is known as the Bridgman–Stockbarger method, and can be carried out in both the horizontal and the vertical variants. The apparatus needed for the Bridgman–Stockbarger process is basically of simple design. Difficulties arise in the choice of suitable container materials, or in the special treatment of the surface of the container which is in contact with the melt.

The normal directional freezing method (after Bridgman) is commonly used for the synthesis, purification, and doping of compounds which do not decompose, in both the horizontal and the vertical variants [51-54].

Hazelby and Parmee [51] prepared aluminium antimonide by pulling a boat containing the melt through the furnace at 2 mm min^{-1} (horizontal variant). Vertical variants of the normal directional freezing method were used by Lawson [52] and by Harman [53].

Lawson [52] grew single crystals of lead sulphide, selenium, and telluride at rates of 0.017–0.17 mm min^{-1}. Since a sealed container (bulb) is used, the method is not suitable for compounds which expand on solidification, such as indium antimonide, gallium antimonide, and others. Mercury selenide was obtained as a coarsely crystalline ingot by a vertical variant of Bridgman's method [53] at a growth rate of ~0.05 mm min^{-1}.

Crystals of mercury and cadmium telluride were grown [54] at 0.04 mm min^{-1} in a furnace with a temperature gradient, with the charge arranged vertically.

Crystal pulling from melts by the methods of Czochralski and Kyropoulos‡ is also widely used in the preparation, purification, and doping of compounds which do not decompose. The pulling is carried out in the vertical direction, and upwards. Horizontal variants of this method, or vertical variants with downward pull, have not so far been reported.

Large single crystals of indium antimonide have been pulled from the melt by the Czochralski–Kyropoulos method [2,56,57]. A quartz crucible was used.

Mirgalovskaya and Matkova [58] prepared single crystals of indium antimonide by Czochralski's method using a quartz crucible. The pulling rate was 0.7–0.8 mm min^{-1}, and the crucible and the seed were rotated at 4–5 revolutions per minute and 3–4 revolutions per minutes respectively.

Single crystals of aluminium antimonide were prepared by pulling from the melt in an apparatus originally designed for the growth of germanium and silicon single crystals. Using graphite or sintered alumina crucibles [59-61], Mirgalovskaya and Strel'nikova [62] prepared single crystals of aluminium antimonide by Czochralski's method. With alumina crucibles and a helium atmosphere, the pulling rate was 0.7 mm min^{-1}, and the seed and the crucible were rotated at 2 revolutions per minute in opposite directions.

Zone melting is a very popular method of synthesising, purifying, and doping semiconducting compounds [5,6,63].

Indium antimonide was zone-melted in quartz boats in order to purify and to homogenise it, using an argon atmosphere [64], vacuum [65], and vacuum with electromagnetic stirring of the molten zone [66]. Mirgalovskaya and Matkova [58] zone-melted indium antimonide at a crystallisation velocity of 0.2 mm min^{-1}, and obtained large-grained specimens containing 10^{16} cm^{-3} impurity atoms, and having an electron mobility of 82 500 cm^2 V^{-1} s^{-1} at 300°K. Vinogradova *et al.* [67] investigated the purification of indium antimonide by zone melting. Their ingots were 150–350 mm long and 4–7 mm in diameter. The length of the molten zone was 5–50 mm, the rate of crystallisation 0.1–1 mm min^{-1}, and the number of zone passes as high as 45. The result was

† This technique is called "floating-zone" melting in the English and American literature (Ed. of Translation).

‡ Kuznetsov points out [55] that crystal growth from the melt can be carried out by Czochralski's method (the growing crystal is pulled upwards, and simultaneously rotated about its longitudinal axis) and by Kyropoulos' method (the seed remains stationary, and crystal growth proceeds only as a result of the loss of heat from the charge). Some non-Soviet authors [1,6,56,57] fail to make a clear distinction between these principles of crystal growth.

indium antimonide of the highest reported purity: $2.5 \times \times 10^{13}$ cm^{-3} impurity atoms, and an electron mobility of 400 000 $cm^2 V^{-1} s^{-1}$ at 77°K and 100 000 $cm^2 V^{-1} s^{-1}$ at 300°K.

Gallium antimonide crystals have been prepared[68-70] by direct fusion followed by zone melting. The preparation of aluminium antimonide single crystals by zone melting has also been reported[60,71-73].

All the examples so far discussed refer to zone melting in its horizontal variant, with a container. Crucible-free vertical variants do not appear to have been used, probably because of the high density of semiconducting compounds, coupled with a low surface tension in the molten state, which limits the ingot diameter to 4–6 mm. An analogous situation exists with germanium. Vertical zone-melting methods with a container have not been applied, either because the compounds were too reactive or because of large volume changes on solidification.

In one case, bismuth telluride crystals have been prepared by zone melting in a vertical, sealed quartz tube[74], with a zone 1–2 cm long travelling at 1.0–1.4 mm min^{-1}.

Methods of preparation of congruently melting compounds by crystallisation from non-stoichiometric melts are of interest. Fisner *et al.*[75] obtained single crystals of zinc antimonide by the horizontal form of Bridgman's method in a graphite boat which could be moved along a tube of Vycor glass. The temperature gradient at the solidifying interface was ~ 4 deg mm^{-1}, and the velocity of crystallisation (caused by the motion of the temperature field) was ~ 0.06 mm min^{-1}. Zone melting was used in the same investigation[75] to grow single crystals on a seed, with a 25 mm zone length, a zone temperature of 560–575°, and a crystallisation velocity of ~ 0.18 mm min^{-1}. In both cases crystallisation was carried out from melts of composition 40 at.% Zn + 60 at.% Sb.

Compounds which melt at low temperatures without decomposition are seldom prepared by crystallisation from a non-stoichiometric melt. This method has been used mostly for the preparation of infusible compounds such as silicon carbide (β-modification)[76-81].

A solution of carbon in silicon, prepared by melting the latter in a graphite crucible, is used. We may consider, as an example, the work of Smith[76]. A graphite crucible with lid, containing the molten silicon, was heated to 1600–2200°, with a temperature gradient of 15–36° along the length of the crucible. The process was carried out either in a stream, or under pressure (up to 55 atm) of an inert gas. The melt was then cooled at 1.5–30 deg h^{-1}. The crystals were deposited at the bottom of the crucible, where the temperature was lowest.

Another technique for growing crystals of high-melting compounds relies on crystallisation from solution in a "third" component. Solutions of silicon carbide in iron, nickel, and other metals have been used for this purpose[77,78]. Halden[80] grew silicon carbide crystals by the Czochralski method from a solution of carbon in a melt of 65% Fe + + 35% Si. Large aggregates of crystals were obtained with the melt at 1675–1750°, the seed at 1665°, and a crystallisation rate of 0.06–0.36 mm min^{-1}. Better results were achieved by rotating the graphite crucible. Ellis[81] grew silicon carbide crystals from solutions of SiC in iron, nickel, or silicon, by cooling a quartz crucible containing the melt at 100 deg h^{-1}. The crystals, which had dimensions of the order of 2.5 mm, were isolated by dissolving the matrix in nitric or hydrofluoric acid.

5. METHODS OF PREPARATION OF SEMICONDUCTING COMPOUNDS PRONE TO DECOMPOSITION

Methods without Pressure Control

When a need for new materials (arsenides, phosphides, etc.) with high melting points and dissociation pressures arose in semiconductor physics and semiconductor device technology, the methods of synthesis, purification, doping, and crystal growing described in the preceding sections did not lead to the desired results. It was found possible to grow small crystals in the laboratory, and to study their physical and electrical properties, but the synthetic methods did not lend themselves to application on an industrial scale.

Initially, experiments on the synthesis of compounds which decompose on heating used the same conditions as those used earlier for stable compounds. A sealed tube containing the components of the desired compound was placed in a single-zone (one-temperature) furnace. These methods, like the other methods of preparation of semiconducting compounds without control of the pressure above the melt, require extremely slow heating rates.

The synthesis of a semiconducting compound (indium phosphide) which decomposes on melting, by direct fusion of the initial components, was first attempted[82] in 1941. However, in spite of very long reaction times, a homogeneous compound could not be prepared by melting together indium and phosphorus in sealed bulbs.

With compounds of appreciably lower vapour pressure (arsenides), very prolonged experiments of this type eventually proved successful.

Landelli[82] prepared specimens of indium arsenide by heating stoichiometric mixtures of indium and arsenic for a long time in sealed quartz tubes. Evans and Jaffe[83] obtained gallium arsenide by the same method.

When these tubes are heated, a solid crust of the compound, crystallised from the melt at a temperature below its melting point, is formed on the surface of the liquid charge. This inhibits the diffusion of the vapours of the volatile constituents of the melt, and lengthens the time required for the synthesis. In order to speed up the synthesis, shaking[84,85], vibration[16,86], and rotation[87] of the tube have been tried, in the hope of fracturing the crust of compound and thus facilitating diffusion.

Borshchevskii[16,86] created more favourable conditions for the synthesis of various $A^{III}B^{V}$ compounds liable to decomposition, and of solid solutions of such compounds, by applying low-frequency vibrations from a magnetostrictive device.

Shafer and Weiser[87] prepared indium phosphide by the direct fusion of a mixture of indium and finely divided phosphorus in a sealed quartz tube, which was rotated at 60 revolutions per minute in a horizontal furnace. The purpose of rotating the tube was to prevent the formation of a crust on the surface of the reaction mixture. When the temperature was slowly raised to 820° over a period of 48 h, a porous microcrystalline mass of indium phosphide was obtained. Methods of preparation of decomposable compounds in which pressure control is not provided (single-zone, or single-temperature methods) often produce a mixture of the desired compound with an excess of one of the components, or with the corresponding eutectic. Special methods may be needed to separate the stoichiometric compound from such a mixture, *e.g.* the method of

Wolff *et al.*[88], who prepared single crystals of indium phosphide by normal directional crystallisation of indium-rich indium–phosphorus melts. Crystals of indium phosphide up to 12 mm long and 1.5 mm thick were isolated after removing the excess of indium with a solution of hydrochloric acid in glycerol at 180°. Not surprisingly, the yield of indium phosphide under these conditions was not high.

Recently, a method of preparation of compounds liable to decomposition has come to the fore, in which the pressure is essentially uncontrolled. The volatility of the compound itself and of its components is significantly depressed by the kinetic effect of a high pressure of inert gas introduced above the melt. In practice, an inert gas pressure about 100 times higher than the equilibrium dissociation pressure is adequate. The method is particularly successful in the preparation of compounds undergoing dissociation to give a high vapour pressure of both components (group $A^{II}B^{VI}$ compounds).

Shternberg *et al.*[89] used this method to prepare lead and zinc sulphide single crystals under 100–200 atm of nitrogen by normal directional freezing, the melt being cooled at 1 deg min^{-1}. The controlled, technological preparation of compounds liable to decomposition became possible as a result of the work of Gans *et al.*[90], who achieved control over the pressure in a tube containing the components of the desired compound by separately controlling the temperature of a condensate of the more volatile constituent (two-region, or two-temperature method).

This method formed the basis of later apparatus and technological procedures for the production of semiconducting compounds with high dissociation pressures.

The theoretical concepts underlying the preparation of semiconducting compounds showing dissociation, including phase equilibrium studies, the influence of external pressure on the nature of the interaction between components, the types and the actual forms of the phase diagrams for incongruently subliming compounds, have been discussed by a number of authors[1,87,91-93]. The work devoted to these problems has greatly assisted the search for new methods of preparation of compounds liable to decomposition.

Methods with Control of the Vapour Pressure of the More Volatile Component

Crystallisation methods of preparation of compounds prone to decomposition involving control of the vapour pressure of the more volatile component above the melt can be divided into three groups.

If the vapour pressure of the volatile component within the tube is controlled at the level which enables its solution in the melt to retain a stoichiometric composition, the crystallisation proceeds congruently, *i.e.* the compound is deposited as crystals of stoichiometric composition from a stoichiometric melt.

The vertical variant of the normal directional crystallisation method has not been used any more with these compounds than with compounds which do not decompose, because of the large volume changes on solidification, which tend to break the container.

The horizontal variants have been used by several workers. Harman *et al.*[94] prepared indium arsenide in the apparatus shown diagrammatically in Fig. 4. An evacuated

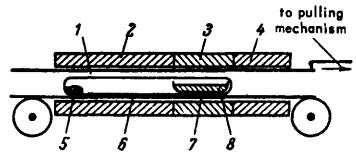

Fig.4. Apparatus for preparing indium arsenide crystals by directional crystallisation (horizontal variant):
1) evacuated and sealed quartz ampoule;
2) furnace set for 560°;
3) furnace set for 1000°;
4) furnace set for 900°;
5) condensate of the more volatile component (arsenic);
6) refractory tube (mullite);
7) quartz boat;
8) indium arsenide melt.

quartz bulb, containing the melt, was drawn through a series of heaters kept at 560°, 1000°, and 900°. The first of these controlled the arsenic vapour pressure in the tube at the desired value (0.33 atm). The second kept the charge in the molten state. The third was intended to relieve the stresses in the crystal. The pulling rate was 0.3–0.8 mm min^{-1}.

Harada and Straust[95] used essentially the same method to prepare indium arsenide single crystals, but they coated their quartz boat with graphite, and conducted the crystallisation at ~ 0.05 mm min^{-1} in a temperature gradient of 18 deg cm^{-1} at the solidification front.

Cunnell *et al.*[96] and Weisberg *et al.*[97] applied this method to the preparation of gallium arsenide.

Compounds have also been prepared by pulling from a melt of stoichiometric composition in a two-zone (two--temperature) furnace. These are best discussed from the standpoint of the constructional features of the particular apparatus employed.

The first such apparatus was described by Gremmelmaier[98], who pulled his crystals in a vertical, evacuated quartz tube located in a two-zone furnace. The seed was raised, and rotated, by means of external magnets which reacted on an iron core within the tube. An apparatus of this type, used in a later investigation[97] for the preparation of gallium arsenide single crystals, is shown in Fig. 5.

Richards[99] described a different design of an apparatus for seed-pulling from the melt of semiconducting compounds liable to decompose. Instead of a sealed tube, he used a hydraulic seal of liquid metal (gallium or indium). The internal pressure was balanced by a controlled external gas pressure. The apparatus was intended for the preparation of indium and gallium arsenide crystals. This construction does not appear to have been widely used.

The next development was a design by Moody and Kolm[100], who relied on the "syringe" seal (Fig. 6) which subsequently became very popular in floating-zone melting as well as in crystal pulling apparatus[97,101,102]. The principles of zone--melting decomposable semiconducting compounds were first established by Boomgard *et al.*[103] The walls of the tube, containing the components of the desired compound or the compound itself, are heated to the temperature at which the vapour pressure of the more volatile constituent is the

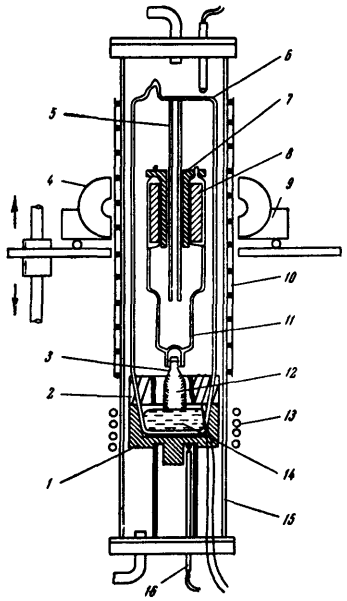

Fig.5. Magnetic-drive apparatus for preparing single crystals of gallium arsenide by pulling from the melt:
1) graphite crucible;
2) transparent heated screen;
3) seed;
4) permanent magnet;
5) quartz guide tube;
6) evacuated and sealed quartz tube;
7) graphite bush;
8) soft-iron cores;
9) magnet rotating mechanism;
10) external heater for tube walls;
11) quartz coupling with seed holder;
12) growing crystal;
13) high-frequency induction coil;
14) melt; 15) external quartz tube filled with inert gas; 16) thermocouple.

same as its vapour pressure over the melt. The liquid zone is kept at a temperature slightly above the melting point of the compound.

Since it is difficult, in practice, to keep the temperature at a constant level over the whole length of the tube (in single-crystal growing, for example), the condensate of the volatile component (see Fig. 4) is transferred to a separate, independently heated part of the tube. The temperature of this part of the tube must be controlled with high precision.

The horizontal variant of zone melting has been used to prepare compounds which tend to decompose [96,104,105].

Cunnell *et al.*[96] purified gallium arsenide by this technique, using high-frequency currents to heat the molten zone. Effer[104] purified gallium arsenide by induction heating, at a rate of crystallisation of 0.6–0.7 mm min^{-1}.

Richards[105] described an interesting horizontal zone-melting procedure, combining purification of gallium arsenide with single-crystal growth. A tube containing the charge was placed inside an alundum tube, heated by an internal winding. A thermally insulating block of firebrick, externally located, could be moved along the tube. The temperature inside this block reached ~1240° when the

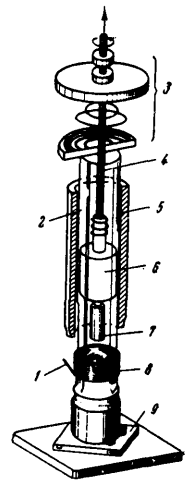

Fig.6. "Syringe" seal apparatus for preparing gallium arsenide single crystals by pulling from the melt:
1) high-frequency induction coil;
2) quartz chamber;
3) coupling seal; 4) coupling;
5) heater for tube walls;
6) quartz piston, internally ground to the chamber wall;
7) seed; 8) crucible with melt;
9) supporting platform.

tube was heated to 800°. The vapour pressure of arsenic inside the sealed tube was controlled by a separate heater.

Vertical zone melting of semiconducting compounds which decompose is carried out without a crucible. Two types of apparatus can be used.

Whelan and Wheatley[106] arranged the ingot within the tube so that the upper part was supported and the lower part was clamped. After the molten zone had been established, the distance between the upper and the lower part of the ingot was kept constant. A similar method was used by Cunnell *et al.*[96], Weisberg *et al.*[97], and Cunnell and Wickam[107] (for gallium arsenide), and by Frosch and Derick[108] for gallium phosphide.

Cunnell and Wickham[107] include the "syringe" seal principle in their apparatus, which enabled them to control the outline of the molten zone. The material zone-refined was gallium arsenide.

Use of Balancing Pressure

The methods and apparatus so far described have been used mainly for arsenides, whose dissociation pressures can be withstood by quartz tubing. However, the strength of quartz tubing proved insufficient for zone-melting phosphides, and balancing pressures had to be applied.

Balancing pressure is used for two purposes: to support the walls of the ampoule[108] and to hinder the diffusion of the volatile component through a seal[109].

Frosch and Derick[108] zone-melted gallium phosphide in a thick-walled steel autoclave inside which were two furnaces

for heating a sealed quartz tube. The latter contained a quartz or graphite boat, centrally located by two lengths of quartz tubing, and could be moved by means of a rod passing through a sliding seal. The molten zone was generated by a high-frequency induction heater.

Fischer[109] described the melting and normal crystallisation of gallium and boron phosphides in autoclaves. The high external pressure suppressed the diffusion of the volatile component out of the ampoule through a narrow (capillary) vent.

Crystallisation from Non-Stoichiometric Melts

Compounds can be prepared from non-stoichiometric melts replenished either through the vapour phase or by a condensed phase. There are many examples[110-115] of the preparation of crystalline compounds by the horizontal, normal directional freezing method.

Crystallisation from a non-stoichiometric melt depletes the melt of one of its components. This can be easily fed back into the melt by dissolution from the vapour phase by means of a condensate of this component in the free volume of the reaction bulb[1,91].

Harman and coworkers[110] prepared indium phosphide by crystallisation of non-stoichiometric melts of indium and phosphorus (35 at.% P) in a three-zone furnace similar to the one shown in Fig. 4. However, crystallisation was induced not by moving the boat through the composite furnace used to generate the required temperature gradients, but by causing the whole temperature profile to move relatively to the fixed ingot. This was achieved by decreasing the power supplied to the heaters.

Harman's apparatus[110] has been used, with only slight modifications, by Weisberg *et al.*[97], Nashel'skii and Ostrovskaya[111], and Guire and Weiser[112], who grew crystals of indium phosphide, and by Strambaugh and coworkers[113], who grew gallium phosphide.

A vertical variant of the normal directional crystallisation method is described in a paper by Vieland and Skalski[114], who prepared gallium arsenide crystals from gallium-rich (Fig. 7) or arsenic-rich melts. Melts of the first type, containing 10 at.% of arsenic, were heated to 900° and crystallised at ~ 0.007 mm min^{-1}.

Crystals of indium phosphide were obtained by Harman and coworkers[110] by pulling from a non-stoichiometric melt. The apparatus, which had a magnetic drive, was similar to the arrangement used[98] by Gremmelmaier (Fig. 5). The melt had the composition 35 at.% P. Crystallisation was allowed to proceed at ~ 0.08 mm min^{-1}, with with rotation of the seed at 6 revolutions per minute.

The crystallisation of decomposable semiconducting compounds by zone melting of non-stoichiometric melts has only been attempted in the horizontal variant[111,115-118].

Nashel'skii and Ostrovskaya[111] prepared large-grained ingots of indium phosphide in graphite-coated quartz boats 100–150 mm long, using a 20 mm zone and a rate of crystallisation of 0.5 mm min^{-1}. The melt in the zone contained ~ 40 at.% P, and was kept at 1020° by an electrical resistance heater.

Davis[115] produced gallium phosphide crystals in graphite boats under a phosphorus pressure of 3–20 atm. The molten zone was generated by a high-frequency induction heater, and was advanced at the rate of 0.001–0.01 mm × × min^{-1}.

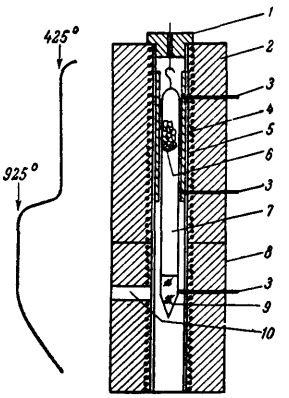

Fig. 7. Apparatus for preparing gallium arsenide crystals by normal directional crystallisation (vertical variant) from non-stoichiometric melts. The temperature profile along the furnace is shown on the left:
1) stopper; 2) low-temperature furnace; 3) thermocouple; 4) steel tube; 5) heater; 6) arsenic; 7) evacuated and sealed quartz ampoule; 8) high-temperature furnace; 9) gallium; 10) inspection window.

Folberth[116] and Nashel'skii *et al.*[117] used zone crystallisation from non-stoichiometric melts in their physicochemical researches. Using this method, Folberth[116] measured the dissociation pressures of compounds (InAs, InP, and GaP) at their melting point by experimenting with liquid zone compositions above and below stoichiometry. Nashel'skii and coworkers[117] determined the effective partition coefficients of zinc and tin impurities during crystallisation of indium phosphide.

Replenishment of a non-stoichiometric melt in the course of crystallisation from a condensed phase refers to the introduction of crystals of the same compound into the melt. Essentially, this procedure is not so much a method of synthesis as a method of recrystallisation for the purpose of purification, heavy doping, or single crystal preparation. Replenishment of the melt by crystals of the desired compound is a "more powerful" method, to use technological jargon, since it minimises the difference in composition between the crystals entering and those leaving the melt.

Fig. 8 shows Trumbore's method[118] of preparing single crystals of semiconducting compounds from a non-stoichiometric melt replenished from a condensed phase. The melt for growing gallium phosphide was kept at 700–800°, and produced aggregates of small crystals. Gallium arsenide crystals were also grown by this method.

As an alternative to adding feed crystals, a non-stoichiometric melt can be kept at constant composition during crystallisation by removing the excess of one of the components (the more volatile) by evaporation. As an example we may quote the work of Lorenz[119], who prepared cadmium telluride crystals from cadmium-rich (69 at.% Cd) melts. A sealed quartz tube, containing the melt in a

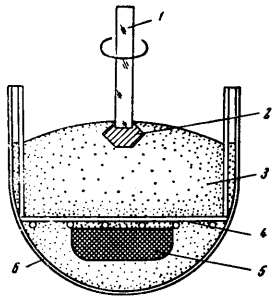

Fig.8. Apparatus for growing crystals of semiconducting compounds from non-stoichiometric melts, with replenishment from a condensed phase:
1) seed rod; 2) growing crystal;
3) gallium–gallium phosphide melt;
4) quartz mesh; 5) feed crystal;
6) quartz crucible.

graphite boat (125 mm), was pulled through a two-zone furnace. As the boat was gradually transferred from the zone at 970° to the zone at 1026° at 1.2 mm h^{-1}, some cadmium evaporated, producing a polycrystalline crop of cadmium telluride. The cadmium vapour was condensed in a zone at 953° (cadmium vapour pressure = 5.9 atm).

6. GENERAL EVALUATION OF THE METHODS OF PREPARATION OF SEMICONDUCTING COMPOUNDS

This review of the preparative methods for semiconducting compounds is arranged in accordance with the classification suggested in Section 2. Individual subgroups have been illustrated by reference to the most typical examples, chosen from the numerous methods described in the literature.

Some of the subdivisions of this classification are arbitrary, and were introduced only because of the distinctive design features of the apparatus employed. For example, there is no real difference in principle between zone melting and normal directional crystallisation with replenishment by a condensed phase, as applied to the preparation of decomposable crystals from their non-stoichiometric melts. When the compound is crystallised from a non-stoichiometric melt containing an excess of the more volatile component, the method becomes a simple one-temperature procedure, and is carried out without controlling the pressure over the melt.

No clear demarcation can be made between methods for preparing compounds without control of the partial pressure of components over the melt but under a pressure of inert gas, on the one hand, and methods of preparation of compounds using a balancing pressure to suppress the diffusion of the more volatile component through a vent, on the other hand. It is also difficult to assign to any particular subdivision of the classification, Stone's novel method[120] for preparing epitaxial gallium phosphide films on gallium arsenide substrates, by diffusional replacement of arsenic by phosphorus atoms. This process was carried out in quartz ampoules in which a phosphorus vapour pressure of 15–20 atm was maintained with a substrate temperature of 800–900°. Technologically, the process is not very different from sintering, but it is essentially an indirect method.

Other methods having a great deal in common are crystallisation from solution in a "third" component and synthesis by condensation in an inert gas stream, synthesis in a stream of one of the components and crystallisation from a non-stoichiometric melt, and so on.

The terminology used to describe the methods of preparation of semiconducting compounds was adopted from the original sources whenever possible, but in many cases we had to resort to literal translation. Therefore, some of the terms used may be slightly unfortunate, but they can undoubtedly be improved by discussion.

To complete this survey of the methods of preparation of semiconducting compounds, it may not be out of place to mention some new methods which, though theoretically possible, have not yet been put to experimental test.

First of all, floating-zone melting (vertical variant) methods are very difficult to apply in practice to semiconducting compounds, on account of their low surface tension and high density. Yet, floating-zone techniques with electromagnetic levitation, "caged"-zone melting[63], and other similar procedures have already been developed for germanium, silicon, and some high-melting metals. Measured such as these should make it possible to apply vertical floating-zone melting to the crucible-free synthesis, purification, and single-crystal growth of compounds, particularly thermally stable ones.

There are no reported instances of the growth of decomposable semiconducting compounds from molten salt solutions. It should be possible, for example, to use the halides of the appropriate metals, or other melts, to prepare solutions of the arsenides and phosphides of Group III (second subgroup) elements, and of the sulphides, selenides, and tellurides of Group II (second subgroup) elements.

The use of a balancing pressure to support the wall of the reaction tube has not been widely applied, as a design feature, to the numerous methods of directional crystallisation from stoichiometric and non-stoichiometric melts. In general, balancing pressure could advantageously be used in all crystallisation methods of preparation of compounds having high dissociation pressures on melting.

Unfortunately, no horizontal methods for growing crystals of compounds from the melt have been developed. These would offer important advantages from the point of view of the removal of impurities from the crystallisation front.

Semiconductor technology is making increasingly stringent demands of chemists and metallurgists for the preparation of semiconducting compounds of higher purity and specified properties. We can therefore expect to witness very rapid developments in semiconductor metallurgy — the science of the preparation of semiconducting compounds — in the near future. The methods and apparatus needed to satisfy the demands of contemporary semiconductor technology will result from the cooperation between research and production staff and academics, engineers, and apparatus designers and fitters.

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THIOLACTONES

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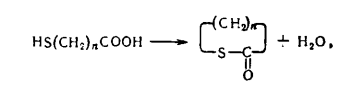
Thiolactones are internal esters of mercapto-acids. The first representatives of this class of sulphur-containing cyclic compounds were obtained towards the end of the last century. Until recently only γ- and δ-thiolactones were investigated. In 1955 β-propiothiolactone was obtained for the first time and in the same year the preparation of the simplest three-membered α-thiolactone was reported but its structure was not proved[1]. Thiolactones with rings larger than six-membered appear to be unknown.

The latest data on the structure of 2-hydroxythiophens, which are actually unsaturated γ-thiolactones, are very interesting.

The reactivity of various thiolactones is of exceptional theoretical and practical interest. Its investigation led to important findings about ring stability and bond conjugation and many new synthetic methods have been developed for mercapto-acids, amino-mercapto-acids, polypeptides containing mercapto(sulphydryl)-groups, antiradiation preparations, and new sulphur-containing polymers. Many of these classes of compounds play an important role in metabolism and exhibit interesting physiological activity.

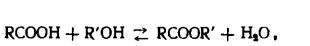
1. SATURATED γ- AND δ-THIOLACTONES

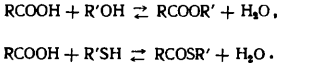
All the known synthetic methods for δ-thiolactones can be used also for γ-thiolactones, but the latter are often obtained in other ways which are unsuitable for δ-thiolactones. Since the properties of saturated γ- and δ-thiolactones are very similar, it is useful to consider them together. The most widely used method for the preparation of saturated γ- and δ-thiolactones is the direct lactonisation of γ- and δ-mercapto-acids



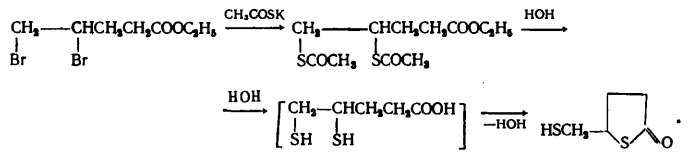
where n = 3 or 4.

"Thiolactonisation" is achieved less readily than the lactonisation of the corresponding hydroxy-acids, which usually do not exist in a free state because of the ease of cyclisation. This is consistent with the fact that the equilibrium in the esterification of acids with alcohols is displaced towards the formation of the ester to a greater extent than in the esterification of acids with mercaptans:



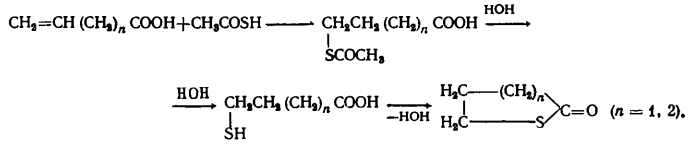


The lactonisation of mercapto-acids is accelerated by heating and in the presence of acids. Branched-chain mercapto-acids are more readily lactonised than acids with a straight chain. Five-membered γ-thiolactones are more readily formed than six-membered δ-thiolactones. This is particularly clearly seen, for example, with γδ-dimercaptovaleric acid, which cannot be isolated in a free state because of its ready cyclisation into the γ-thiolactone[2]. On the other hand, the δ-thiolactone cannot be obtained:



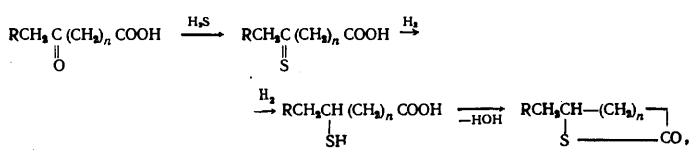
Other examples of partial or complete lactonisation of γ-mercapto-acids directly on preparation are also known. While the lactonisation of δ-mercapto-acids requires prolonged heating at a high temperature (about 270°), the preparation of γ-thiolactones often involves no more than the preparation of the γ-mercapto-acids, whose slow distillation above 100° results in lactonisation.

The most widely used general method for the preparation of γ- and δ-mercapto-acids, which consists in the addition of thioacetic acid to βγ- and γδ-unsaturated acids under free radical conditions, was proposed by Holmberg and Schjånberg[3]. Alkaline hydrolysis of the γ- and δ-acetylthio-acids formed under these conditions yields the corresponding mercapto-acids which can then be lactonised, for example:



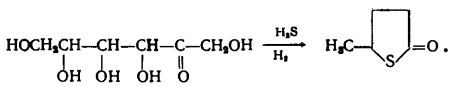
The γ- and δ-thiolactones obtained by this method are listed in the Table.

Farlow and coworkers[10-12] proposed a convenient method for the synthesis of γ- and δ-mercapto-acids, which consists in the hydrogenation of carboxylic acids, containing a thiocarbonyl group in the γ- or δ-position, in the presence of catalysts — sulphides of molybdenum, iron, etc. Usually one starts with keto-acids which are hydrogenated in the presence of hydrogen sulphide, carbon disulphide, or sulphur (reductive thiolation). Application of this method to levulinic, γ-oxopimelic, and γ-acetylbutyric acids yielded the corresponding mercapto-acids, which under the conditions of the reaction are almost completely converted into the γ- and δ-thiolactones:



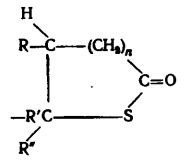
where $n = 2$ and R = H or CH_2COOH, or $n = 3$ and R = H.

The formation of γ-methyl-γ-butyrothiolactone in reductive thiolation of D-fructose has also been described[13]:



The mechanism of this reaction is obscure.

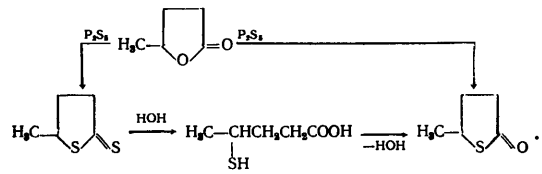
TABLE.



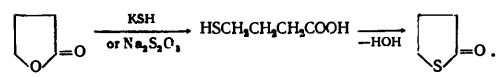
n	R	R′	R″	References
1	H	H	$CH(CH_3)_2$	4
1	H	CH_3	$CH(CH_3)_2$	4
1	H	H	CH_3	5
1	COOH	H	H	6
1	H	H	H	3,7
1	H	H	C_2H_5	8
2	H	H	H	5,8,9
2	CH_3	CH_3	CH_3	4

A method has also been proposed for the conversion of γ- and δ-lactones into the corresponding thiolactones by heating with carbon disulphide[14] or derivatives of thiocarbonic acid[15] [CS_2, COS, $CS(NH_2)_2$, and others], but it does not always give satisfactory results[16,17].

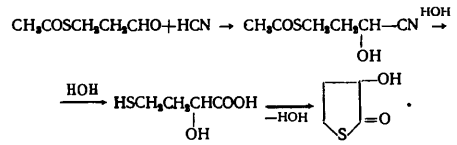
Yur'ev[18] achieved the reaction between γ-butyrolactone and hydrogen sulphide at 350° over alumina and obtained γ-butyrothiolactone in high yield. The conversion of γ-methyl-γ-butyrolactone into a mixture of γ-methyl-γ-butyrothiolactone and γ-methyl-γ-butyrodithiolactone on heating with phosphorus pentasulphide has been described; γ-methyl-γ-butyrodithiolactone yields γ-mercaptovaleric acid on alkaline hydrolysis, the latter being subsequently converted into the γ-methyl-γ-butyrothiolactone[19]:



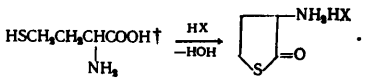
By cleaving γ-butyrolactone with potassium hydrogen sulphide, Reppe *et al.*[20] isolated γ-mercaptobutyric acid, which they dehydrated to γ-butyrothiolactone. Kharasch[21] obtained the same result on cleaving γ-butyrolactone with sodium thiosulphate; in this case the first stage is the formation of Bunte's salt:



The lactonisation of substituted γ-mercapto-acids takes place even more readily than that of γ-mercaptobutyric acid. It has already been pointed out that γδ-dimercaptovaleric acid spontaneously cyclises into γ-mercaptomethyl-γ-butyrothiolactone (see above). α-Hydroxy-γ-mercaptobutyric acid cyclises just as easily[22]:

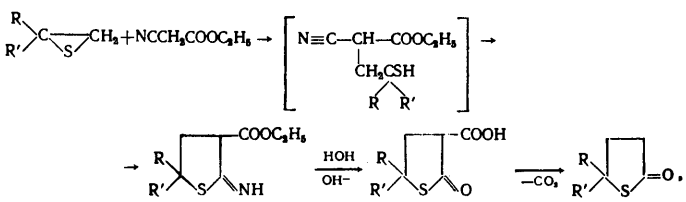


In the presence of acids homocysteine readily forms α-amino-γ-butyrothiolactone [23,24]:



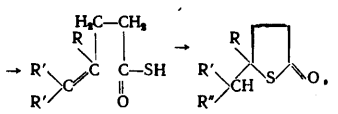
N-acylated homocysteine thiolactone can be obtained similarly or by acylation of homocysteine thiolactone itself [25].

Snyder and Alexander [28] proposed a novel method for the preparation of γ-thiolactones from thioepoxides and cyanoacetic ester:



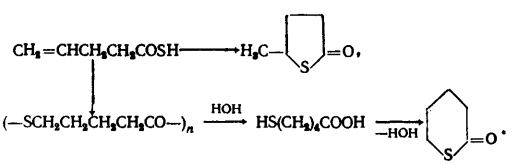
where R = R′ = H, R = H and R′ = CH_3, or R = R′ = CH_3. [29]

Korte and Christoph [4] found that γδ-unsaturated carbothiolic acids spontaneously cyclise into γ-thiolactones:

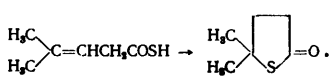


where R = H and R′ = R″ = CH_3, R = R′ = R″ = CH_3, and R = R′ = R″ = H. The analogous isomerisation of unsaturated carboxylic acids takes place under more severe conditions, contrary to the usual finding that lactones are formed more readily than thiolactones. δ-Thiolactones cannot be obtained in this way.

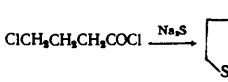
In addition to γ-methyl-γ-butyrothiolactone, allylthioacetic acid yields a linear polythioester, whose hydrolysis leads to the formation of δ-mercaptobutyric acid, which lactonises into δ-valerothiolactone [4]:



The cyclisation of βγ-unsaturated carbothiolic acids has been studied in only one case. As with γδ-unsaturated carbothiolic acids, the γ-thiolactone was obtained [4]:

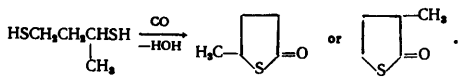


The preparation of γ-butyrothiolactone from γ-chlorobutyryl chloride and sodium sulphide in 71% yield has been described [30,31]:



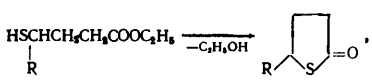
† The initial homocysteine is obtained by demethylation of methionine with hydriodic acid, debenzylation of *S*-benzylhomocysteine with sodium in liquid ammonia [23–26], or by reduction of homocystine [23,27].

When butane-1,3-dithiol reacts with carbon monoxide in the presence of cobalt carbonyl, α(or γ)-methyl-γ-butyrothiolactone forms in 15% yield [32]:



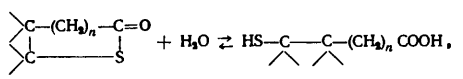
The position of the methyl group has not been established.

Two cases of formation of γ-thiolactones on distillation of γ-mercapto-carboxylic acid esters have been described:



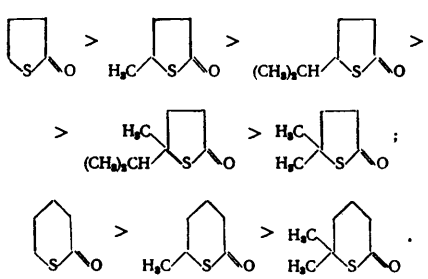
where R = H [7] or R = $CH_2CH_2COOC_2H_5$. [11]

Among the chemical properties of γ- and δ-thiolactones, hydrolysis has been most thoroughly investigated. On hydrolysis of γ- and δ-thiolactones, the ring always splits at the S–acyl bond and the corresponding mercapto-acids are formed. The hydrolysis of γ-thiolactones is reversible while δ-thiolactones are almost completely hydrolysed:



where *n* = 1 or 2. The hydrolysis of γ- and δ-thiolactones is accelerated by acids and especially by bases [5,6,33].

The splitting of substituted thiolactones, including hydrolytic splitting, is more difficult than in the case of unsubstituted thiolactones, *i.e.* the stability of the ring increases with the number of substituents (p. 494). Thus Korte and Christoph [4] found that the rate of alkaline hydrolysis decreases in the following sequences:



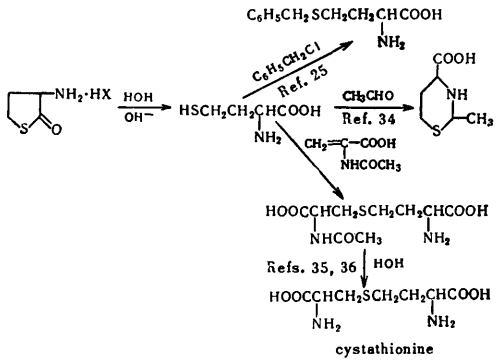
Stevens and Tarbell [29] found that the rate of alkaline hydrolysis of γ- and δ-thiolactones and their oxygen analogues is less sensitive to changes in structure than the rate of hydrolysis of open-chain esters and thioesters. Thus ethyl acetate is hydrolysed 100 times faster than t-butyl acetate. On the other hand, γ-butyrolactone is hydrolysed only eight times faster than γγ-dimethyl-γ-butyrolactone. This relation between the rates of alkaline hydrolysis holds also for thioesters and thiolactones.

The authors' explanation of this finding is that the cyclic structure ensures a relatively fixed position of the carbonyl group, so that the possibility of nucleophilic attack on this group changes little when substituents are introduced in the vicinity of the reaction centre; on the other hand, in esters

and thioesters introduction of substituents gives rise to steric hindrance and impedes the attack of the nucleophilic agent on the carbonyl group.

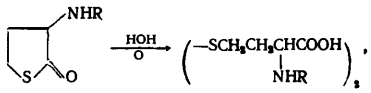
After hydrolysis of substituted γ-thiolactones, it is in many cases impossible to isolate the corresponding γ-mercapto-acids, since on acidification they readily recyclise into the thiolactones [4,20,22,29]. Thus, it is virtually impossible to isolate homocysteine after hydrolysis of homocysteine thiolactone.

The ease of alkaline hydrolysis of homocysteine thiolactone makes it possible to employ it as a source of homocysteine, which is otherwise difficult to obtain:

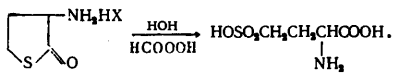


Since homocysteine thiolactone and its *N*-acetyl derivatives are active antiradiation agents‡, studies of the hydrolysis of this substance have a bearing on the problem of the relation between the protective properties of substances and their structure [34,37-41].

Hydrolysis of γ-thiolactones in the presence of oxidising agents yields disulphides of γ-mercapto-acids [28,42,43]. Thus, on alkaline hydrolysis of homocysteine thiolactone in the presence of atmospheric oxygen, homocystine is formed [25]:

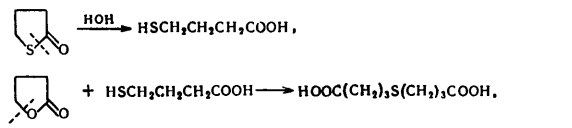


where R = H or COC_6H_5. Hydrolysis of homocysteine thiolactone in the presence of hydrochloric and performic acids gives homocysteic acid [44]:

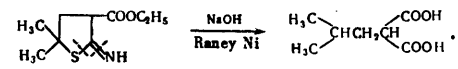


Some reactions of γ-thiolactones and their derivatives can only be understood by assuming that the first stage of the reaction involves hydrolytic opening of the thiolactone ring at the S–acyl bond.

Reppe and coworkers [20,45,46] described the reaction of thiolactones with lactones in the presence of alkali. The authors are clearly wrong in interpreting this reaction as splitting of the thiolactone by the salt of the hydroxy-acid formed on alkaline hydrolysis of the lactone. It is evident that the alkali hydrolyses the thiolactone and the salt of the mercapto-acid thus formed splits the lactone at the O–acyl bond:

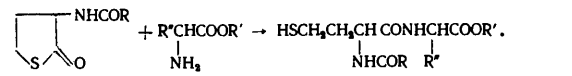


Elimination of sulphur from 3-ethoxycarbonyl-2-imino--5,5-dimethylthiophan with Raney nickel in the presence of alkali [28] gave isobutylmalonic acid:

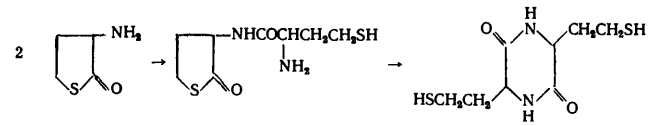


This could only occur after preliminary hydrolytic splitting of the thiolactone ring at the S–acyl bond. Otherwise elimination of sulphur would have given rise to an aldehyde group.

Aminolysis of γ-thiolactones has been investigated with homocysteine thiolactone as an example. *N*-acyl homocysteine thiolactone is split by α-amino-acid esters under mild conditions [42]:

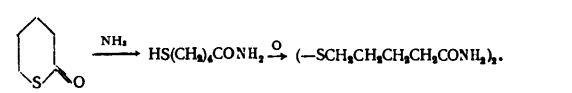


The aminolysis of *N*-acetylhomocysteine thiolactone with glycylglycine and ε-aminocaproic acid has been described [44]. The acylating capacity of *N*-acyl homocysteine thiolactone is used in peptide synthesis and for introduction of sulphur into proteins [47-49]. Homocysteine thiolactone exists only in the form of hydrogen halides or *N*-acyl derivatives. When an attempt is made to obtain homocysteine thiolactone with a free amino-group, mutual aminolysis of two molecules of homocysteine thiolactone takes place with formation of 3,6-di-(β-mercaptoethyl)-2,5-dioxopiperazine [24]:

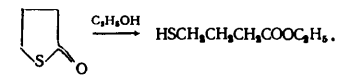


The latter is readily oxidised to a polymeric product.

The aminolysis of δ-thiolactones has been described in only one case: δ-valerothiolactone gave the amide of δ-mercaptovaleric acid, which is readily oxidised to the corresponding disulphide [33]:



The alcoholysis of δ-thiolactones has not been investigated, but the splitting of γ-butyrothiolactone with ethanol in the presence of sodium ethoxide has been described:

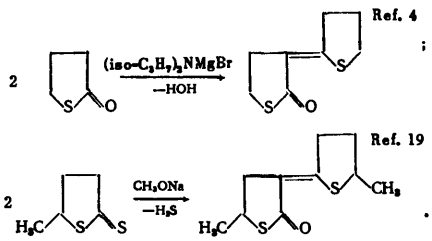


Thus in hydrolysis, aminolysis, and alcoholysis δ- and γ-thiolactones are split at the S–acyl bond.

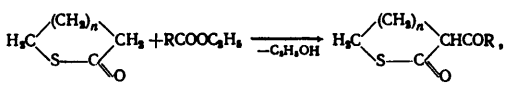
‡ *N*-Carbamoylhomocysteine thiolactone does not exhibit protective antiradiation properties [34].

The reduction of γ-butyrothiolactone to thiophan with zinc amalgam in dilute hydrochloric acid, described by Yur'ev[18], characterises the reactivity of the carbonyl group.

Like γ-lactones, γ-thiolactones and γ-dithiolactones undergo self-condensation in the presence of alkaline catalysts:

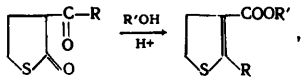


The result of the presence of an active methylene group, γ- and δ-thiolactones, like their oxygen analogues, are capable of undergoing ester condensation in the presence of basic catalysts:

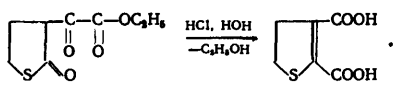


where n = 1 or 2.

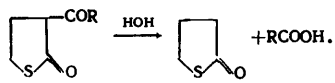
Since γ- and δ-thiolactones are readily split by alkaline reagents, application of the usual Claisen condensation catalysts (C_2H_5ONa, NaH, Na) results in low yields of the condensation products. The best catalyst for the Claisen condensation involving γ- and δ-thiolactones is diisopropylaminomagnesium bromide $(iso\text{-}C_3H_7)_2NMgBr$.[7,9,16] The α-acyl-γ- and α-acyl-δ-thiolactones undergo the so-called acyllactone rearrangement in the presence of hydrogen chloride[4,16,17]. Thus, in the cold in alcohols saturated with hydrogen chloride, α-acyl-γ-thiolactones form esters of dihydrothiophen-3-carboxylic acid in good yields:



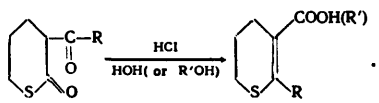
where R = H and R′ = CH_3, R = R′ = CH_3, and R = $COOC_2H_5$ and R′ = C_2H_5. When R = $COOC_2H_5$, the rearrangement takes place also in the presence of hydrochloric acid:



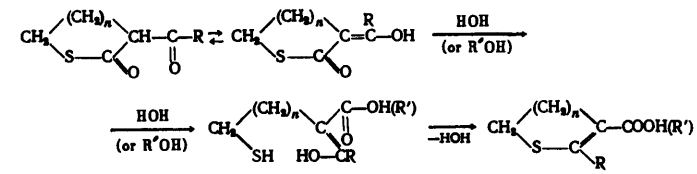
However, when R = H or CH_3, hydrochloric acid causes the acid hydrolysis characteristic of β-keto-esters:



α-Acyl-δ-thiolactones rearrange even more readily than α-acyl-γ-thiolactones. In the presence of hydrochloric acid dihydrothiopyran-3-carboxylic acids are formed and in the presence of alcohol saturated with hydrogen chloride the esters of these acids[16]:

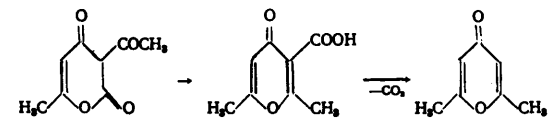


The acyllactone rearrangement is a convenient method for the preparation of dihydrothiophen- and thiopyran-carboxylic acids, which are difficult to obtain. The rearrangement involves the enolisation of the α-acylthiolactone, which is characteristic of β-keto-esters, and solvolytic splitting of the thiolactone ring at the S–acyl bond (hydrolysis or alcoholysis) with subsequent elimination of water[4,17]:

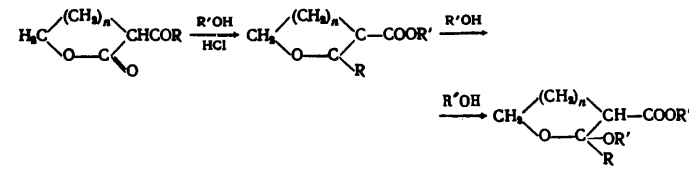


where n = 1 or 2.

The acyllactone rearrangement has also been studied in detail for γ- and δ-lactones. A generally familiar example of the rearrangement of a δ-lactone is the conversion of dehydroacetic acid into αα′-dimethyl-γ-pyrone:



The rearrangement of α-acyl-γ- and α-acyl-δ-lactones in alcohol usually results in saturated systems because of the addition of the alcohol to the double bond:



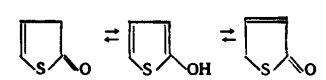
where n = 1 or 2.

However, alcohol does not add to the products of the acyllactone rearrangement of thiolactones either under the conditions of the rearrangement or under more severe conditions. Korte and coworkers explain this difference by the fact that the free electron pair of the sulphur atoms shows a greater tendency towards conjugation with the π electrons of the double bond than the electron pair of the oxygen atom.

2. UNSATURATED γ-THIOLACTONES AND γ-THIOLACTONES CONDENSED WITH A BENZENE RING

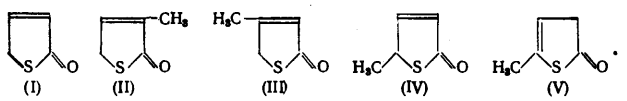
Unsaturated γ-Thiolactones

Unsaturated γ-thiolactones are tautomeric forms of 2-hydroxythiophen:



Infrared and nuclear magnetic resonance spectroscopy showed that 2-hydroxythiophen and its derivatives virtually do not exist in the hydroxy-form[50]. Thus unsubstituted 2-hydroxythiophen exists exclusively as the thiolactone (I), 2-hydroxy-3-methylthiophen consists of virtually the pure

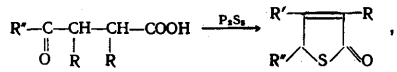
thiolactone (II), and 2-hydroxy-4-methylthiophen also exists only as the unsaturated thiolactone, the double bond being located between positions 3 and 4 in this case too[51] [thiolactone (III)]. Both thiolactone forms [(IV) and (V)] of 2-hydroxy-5-methylthiophen were isolated and their interconversion was achieved. The hydroxy-form of any of the above compounds could not be isolated.



(I) (II) (III) (IV) (V)

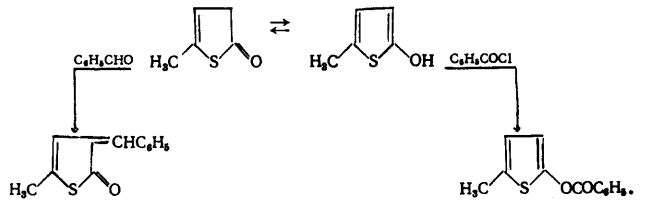
Only in the case of 2-hydroxy-5-phenylthiophen was the hydroxy-form detected spectroscopically in alcohol solution[52]. Clearly, the reason for the stability of the hydroxy--form in this case is the formation of a conjugated system with the benzene ring and the high polarity of the solvent. In chloroform solution of 2-hydroxy-5-phenylthiophen the hydroxy-group can no longer be detected, and only the carbonyl group is found. Probably, 2-hydroxy-5-phenylthiophen exists as a tautomeric equilibrium mixture, the equilibrium being displaced towards the hydroxy-form in polar solvents. Thus 2-hydroxy-5-phenylthiophen is the only 2-hydroxythiophen whose generally accepted name to some extent corresponds to its structure. In all other cases one should refer to unsaturated γ-thiolactones rather than 2-hydroxythiophens. It is in fact the inability of "2-hydroxythiophen" to exist in the hydroxy-form that is responsible for the profound difference between the properties of these and phenols. While the physical properties of 2-methoxythiophen and anisole are as similar as those of thiophen and benzene, "2-hydroxythiophen" and phenol differ sharply from one another in both physical and chemical properties[53]. In contrast to phenols, "2-hydroxythiophens" are unstable and difficult to obtain.

The first attempts to obtain derivatives of "2-hydroxythiophen" were made in the eighties of the previous century. Kues and Paal[54-57] used a method for the preparation of "2-hydroxythiophen" derivatives analogous to the classical synthesis of thiophen from succinic acid and phosphorus trisulphide. By heating together γ-keto-carboxylic acids and phosphorus pentasulphide, the above workers obtained substituted "2-hydroxythiophens" in low yields§:

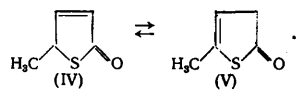


where R = R′ = H and R″ = CH_3, R = R′ = H and R″ = C_6H_5, R = H and R′ = R″ = CH_3, and R = R″ = CH_3 and R′ = H. However, later attempts to repeat these syntheses were not always successful[52].

In 1939 Steinkopf and Thormann[58], in an attempt to prepare "2-hydroxy-5-methylthiophen", modified somewhat the method of Kues and Paal and obtained a substance with a boiling point different from that of the "2-hydroxy-5-methylthiophen" which the earlier workers synthesised. The boiling point of the substance prepared by Steinkopf and Thormann was close to that of *p*-cresol and gave a benzylidene derivative. The above workers therefore decided that they were the first to obtain 2-hydroxy-5-methylthiophen. They explained the formation of the benzylidene derivative on reaction with benzaldehyde by the existence of a tautomeric equilibrium:



It was not until 1960 that Gronowitz and Hoffman[50] succeeded in repeating the experiments of Kues and Paal and established the structure of "2-hydroxy-5-methylthiophen" (thiotenol). They showed that under the usual conditions "2-hydroxy-5-methylthiophen" consists of an equilibrium mixture of two thiolactone forms: 85% of (IV) and 15% of (V):

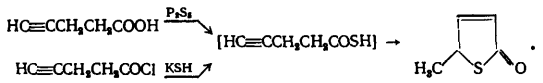


(IV) (V)

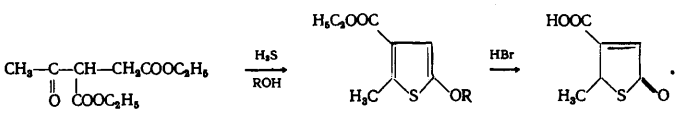
Form (V) is the less stable of the two¶.

Kues and Paal obtained the thiolactone (V) while Steinkopf and Thormann prepared the isomeric form (IV), but uncritical use of chemical reactions for the determination of the structure of "2-hydroxy-5-methylthiophen" led them to an erroneous conclusion†.

"2-Hydroxy-5-methylthiophen" (IV) was also prepared by the isomerisation of but-3-yncarbothiolic acid[60]:

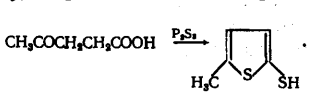


"2-Hydroxy-5-methylthiophen-4-carboxylic acid" was obtained by the action of hydrogen sulphide on the ester of β-ethoxycarbonyllevulinic acid[61]:

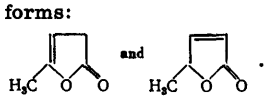


In all the methods for the preparation of substituted "2-hydroxythiophens" considered above the starting materials were open-chain compounds. However, methods

§ Reaction of levulinic acid with phosphorus trisulphide yields 2-mercapto-5-methylthiophen, which exists predominantly in the thiol form[50]:



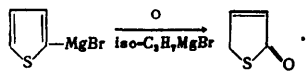
¶ The oxygen analogue of 2-hydroxy-5-methylthiophen also exists in two lactone forms:



The first of these (α-Angelica lactone) is less stable than the second (β-Angelica lactone).

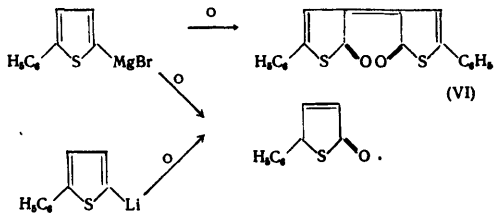
† Demerseman and coworkers[59] assert that "2-hydroxy-5--methylthiophen" contains more than 90% of the unsaturated thiolactone with the double bond between positions 4 and 5 [form (V)], and they completely disregarded the second thiolactone form.

have also been developed for the introduction of a hydroxy--group into the thiophen ring. Thus in 1950 Hurd and Kreuz [53] were the first to obtain unsubstituted "2-hydroxythiophen" by oxidising with oxygen 2-thienylmagnesium bromide in the presence of more than an equivalent amount of isopropylmagnesium bromide:

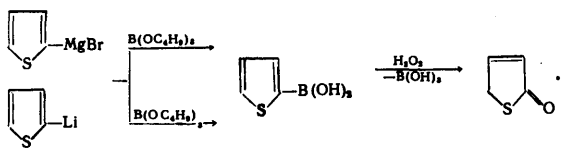


When peroxides are used as oxidising agents, the yield of "2-hydroxythiophen" is reduced [62].

Oxidation of 5-phenylthien-2-ylmagnesium bromide and 5-phenylthien-2-yllithium under the same conditions gave "2-hydroxy-5-phenylthiophen" in 30% yield [63]. The bisthiolactone (VI) was obtained from 5-phenylthien-2-ylmagnesium bromide as a side product:

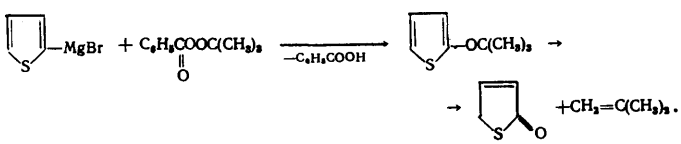


Reaction of thiophen metal-substituted in the 2-position with tributyl borate at -70° yielded 2-thienylboronic acid, whose oxidation with hydrogen peroxide is a convenient method for the preparation of "2-hydroxythiophen" [51]:

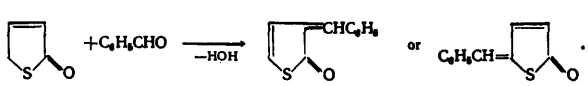


Apart from "2-hydroxythiophen", "2-hydroxy-5-methylthiophen" and the previously unknown "2-hydroxy-3-methylthiophen" and "2-hydroxy-4-methylthiophen" were obtained in good yields by this method.

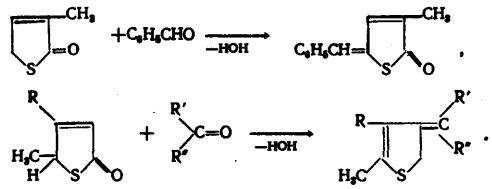
The best method for the synthesis of "α-hydroxythiophen" (70% yield) is pyrolysis of 2-t-butoxythiophen in the presence of *p*-toluenesulphonic acid [63]:



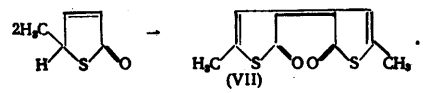
"2-Hydroxythiophens" are very unstable compounds. They readily resinify on being stored in air and undergo particularly rapid decomposition in the presence of alkalis, alcohols, and amines. On the other hand, "2-hydroxythiophen" remains virtually unchanged on being boiled at 219° in a stream of nitrogen [53]. "2-Hydroxythiophens" undergo condensation with carbonyl compounds. For example, with benzaldehyde a benzylidene derivative is obtained:



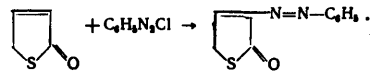
Substituted "2-hydroxythiophens" react similarly with aldehydes and ketones:



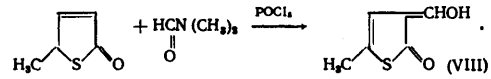
The oxidation of "2-hydroxy-5-methylthiophen" with ferric chloride to the bisthiolactone (VII) has been described [58]:



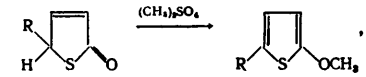
"2-Hydroxythiophen" undergoes azo-coupling [53]:



"2-Hydroxy-5-methylthiophen" reacts with dimethylformamide in the presence of phosphorus oxychloride with the formation of "3-formyl-2-hydroxy-5-methylthiophen"; the product does not give reactions characteristic of the aldehyde group, which appears to favour the thiolactone (VIII) structure [59]:

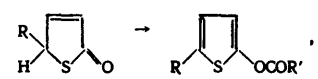


"2-Hydroxythiophens" cannot be alkylated with alkyl halides or diazomethane [52,53,59], but with dimethyl sulphate the corresponding 2-methoxy-derivatives can be obtained from "2-hydroxythiophen" and "2-hydroxy-5-methylthiophen" [53,59]:



where R = H or CH_3.

When acted upon by acylating agents (acetic anhydride, benzoyl chloride), "2-hydroxythiophens" give the acylated derivatives [52,55,58,60]:



where R = H, CH_3, or C_6H_5, and R′ = CH_3 or C_6H_5.

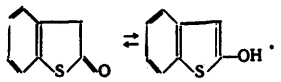
"2-Hydroxythiophens" give a colour with ferric chloride and dissolve in alkalis in the cold. They can be regenerated by passing CO_2 through the alkaline solution, but about 50% of the substance is lost, apparently as a result of ring rupture.

Thus "2-hydroxythiophens" undergo reactions characteristic of the hydroxy-form and both thiolactone forms. However, physical methods as a rule fail to confirm the hypothesis of the tautomerism of "2-hydroxythiophens".

Evidently the dual reactivity of "2-hydroxythiophens" is to be explained by migration of the reaction centre.

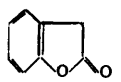
γ-Thiolactones Condensed with a Benzene Ring

Thio-oxindole is a tautomeric form of 2-hydroxythianaphthen:



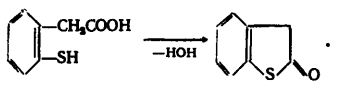
Because of the absence of spectroscopic data, the structure of thio-oxindole is still not completely clear. Two crystalline forms of thio-oxindole melting at 33–34° and 44–45° have been described‡[64]. The data on the interconversion of these forms are very contradictory. However, it is known that, when crystals of a given modification are added to fused thio-oxindole, the form with the required melting point can be obtained[65]. For this reason, the hypothesis[66] that one of the forms is 2-hydroxythianaphthen and the other thio-oxindole is not well founded.

It is most likely that the two forms of thio-oxindole are different crystalline modifications. The oxygen analogue of thio-oxindole, isocoumaranone (IX), also exists in two crystalline modifications:



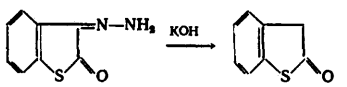
(IX).

Marschalk[67] was the first to obtain unsubstituted thio-oxindole by dehydration of *o*-mercaptophenylacetic acid:



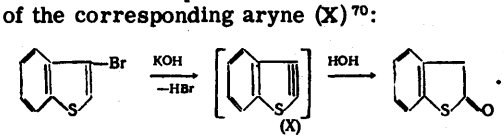
Lactonisation takes place on heating or under the action of dehydrating agents§[67].

Thio-oxindole also forms when the β-hydrazone of thianaphthenquinone undergoes the Kishner reaction[64,65]:



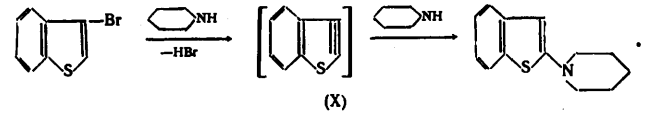
Kommpa[68] obtained thio-oxindole by heating *o*-methylthiophenylacetyl chloride with aluminium chloride in xylene:

The same worker[68,69] described the formation of thio-oxindole as a result of the reaction of 3-bromothianaphthen with alcoholic caustic potash at about 200° and a pressure of 50 atm. The reaction proceeds *via* the intermediate formation of the corresponding aryne (X)[70]:



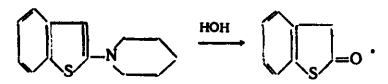
(X)

The same intermediate (X) is formed in the reaction between 3-bromothianaphthen and piperidine[70]:

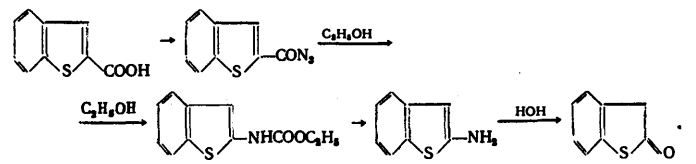


(X)

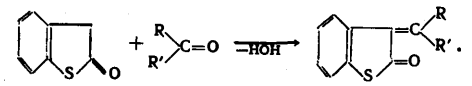
Hydrolysis of the resulting 2-piperidinothianaphthen yields thio-oxindole[71]:



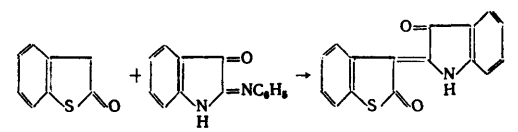
Thio-oxindole can also be obtained from thianaphthen-2-carboxylic acid by the Curtius reaction followed by hydrolysis of the amine formed[72]:



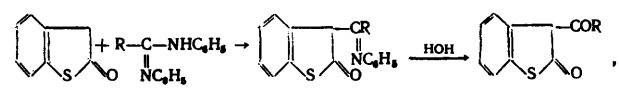
Numerous reactions of thio-oxindole reflect the mobility of the hydrogen atom in position 3.[73,74] Thio-oxindole readily reacts with carbonyl compounds[64,67,75]:



Even easier is the condensation of thio-oxindole with the anils of carbonyl compounds[67,75,76], for example:

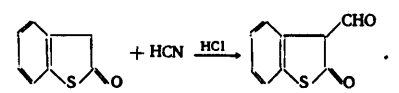


NN'-Diphenylamidines acylate thio-oxindole in position 3:[65]

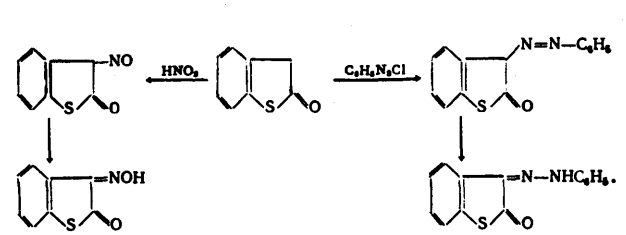


where R = H or CH_3.

3-Formylthio-oxindole was obtained by formylating thio-oxindole by the Gattermann–Koch reaction[65]:



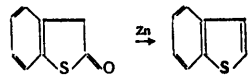
The formation of a nitroso-derivative of thio-oxindole and its azo-coupling with phenyldiazonium chloride has been described[64]:



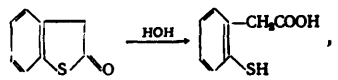
‡ 6-Ethoxythio-oxindole is also known in two forms melting at 39–40° and 47–48°.[65]

§ Because of its ready lactonisation, *o*-hydroxyphenylacetic acid does not exist in a free state[67].

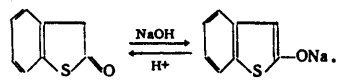
Reduction of thio-oxindole with powdered zinc yields thianaphthen[64]:



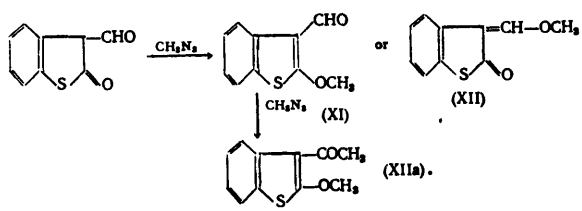
Alkaline hydrolysis of thio-oxindole with heating gives *o*-mercaptophenylacetic acid[67,68,71]:



but thio-oxindole can be regenerated by acidifying the solution after it has been dissolved in cold alkali[64]:

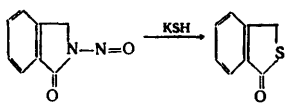


3-Formylthio-oxindole could not be alkylated either with methyl iodide or with dimethyl sulphate. Reaction with diazomethane gave a product with structure (XI) or (XII). A dimethylated derivative, to which structure (XIIa) was ascribed, forms as a side-product[65]:

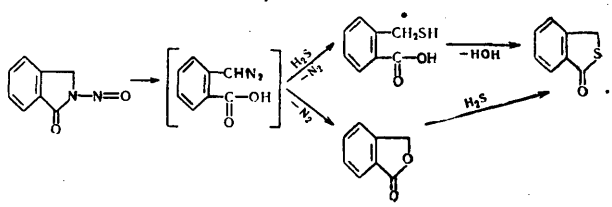


2-Thiophthalide. This γ-thiolactone, condensed with the benzene ring, is an isomer of thio-oxindole, but does not exhibit dual reactivity because of the absence of the hydrogen atom in the α-position with respect to the carbonyl group. It is a normal thiolactone, known in the literature under the name 2-thiophthalide, and was the first γ-thiolactone to be described.

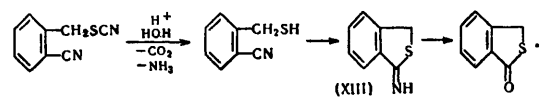
It was first obtained by Graebe[77] by treatment of *N*-nitrosophthalimidine with potassium or sodium hydrogen sulphide:



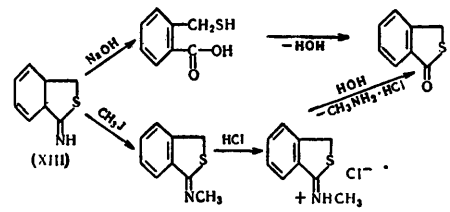
It may be supposed that the reaction involves the intermediate formation of a diazo-compound:



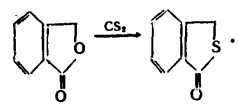
Day and Gabriel[78] obtained 2-thiophthalide by the action of concentrated hydrochloric acid on *o*-thiocyanatomethylbenzonitrile, 1-imino-2-thiophthalide (XIII) being formed as an intermediate:



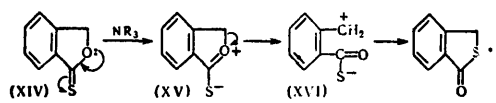
The same workers[78] obtained 2-thiophthalide from 1-imino-2-thiophthalide by other pathways:



A patent[15] describes the synthesis of 2-thiophthalide by heating phthalide with derivatives of thiocarbonic acid [CS_2, HSCN, $CS(NH)_2$, and others] in an alkaline medium:



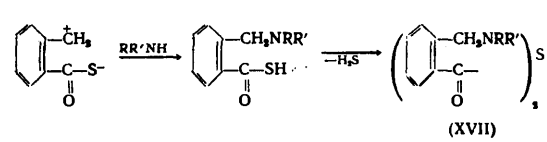
Prey and coworkers[79,80] obtained 2-thiophthalide in high yield by the rearrangement of 1-thiophthalide (XIV) in the presence of amines. They suggested the following mechanism for the rearrangement:



By virtue of its free electron pair, the amine enhances the polarisation of 1-thiophthalide and tends to stabilise the dipolar ion (XV) which undergoes "thermal" ring-opening with the formation of the betain structure (XVI); the latter is then converted to the more stable 2-thiophthalide.

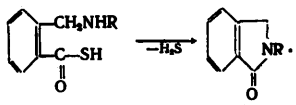
The occurrence of the stage involving the "thermal" formation of the betain (XVI) has been confirmed by measurements of the electrical conductivity of 1-thiophthalide in pyridine. Below 100° the conductivity of the solution remained unchanged and the initial 1-thiophthalide was isolated. At 100° the conductivity increased, after which 2-thiophthalide was isolated from solution.

When secondary amines are used, the betain (XVI) can be stabilised by the addition of the amine, the resulting carbothiolic acid being then converted to the diacylsulphide (XVII):

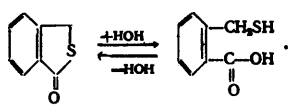


The latter is in many cases isolated as a side-product. When a primary amine or ammonia is used, an *N*-substituted phthalimidine, the product of the intramolecular

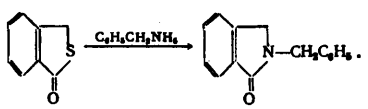
acylation of the amino-group of the carbothiolic acid, is isolated in addition to the diacylsulphide:



The properties of 2-thiophthalide have been very little investigated. Its alkaline hydrolysis yields a γ-mercapto--acid[77], which on heating is reconverted into 2-thiophthalide:

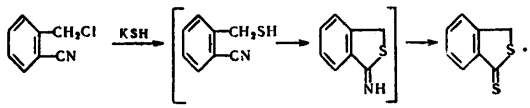


When 2-thiophthalide is heated with benzylamine under pressure, *N*-benzylphthalimidine is obtained[79]:

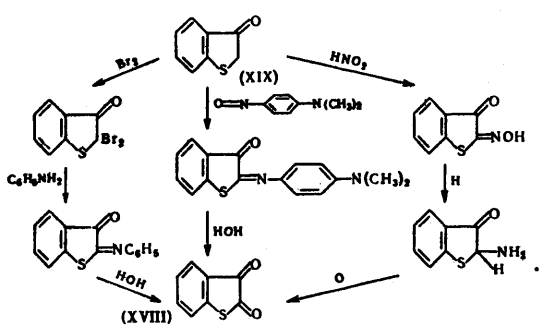


The mechanism of this reaction has not been studied.

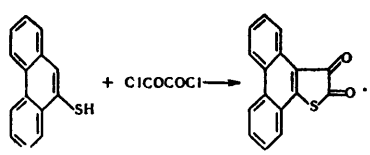
In an attempt to prepare 2-thiophthalide from *o*-cyanobenzyl chloride and potassium hydrogen sulphide, Gabriel and Leupold[81] obtained 1,2-dithiophthalide:



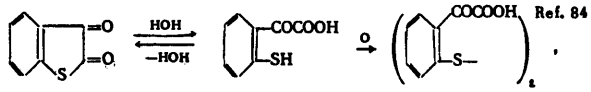
Thianaphthenquinone (XVIII) is α-oxo-γ-butyrothiolactone condensed with the benzene ring. Usually thianaphthenquinone and its derivatives are obtained by indirect oxidation of thioindoxyl (XIX)[82]:

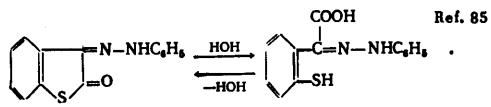


The formation of thianaphthenquinone derivatives from oxalyl chloride and thiophenol derivatives has been described[83], for example:

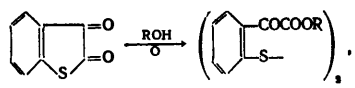


The hydrolysis of thianaphthenquinone and its derivatives involves ring rupture at the S–acyl bond. The γ-mercapto-acids thus formed are readily oxidised to the corresponding disulphides, which on heating are reconverted into the initial thiolactone:

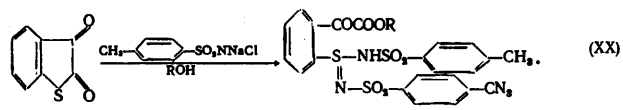




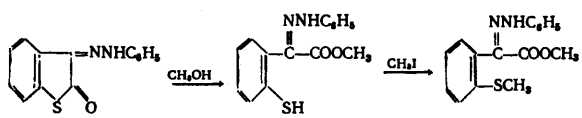
Like the hydrolysis, the alcoholysis of thianaphthenquinone proceeds with ring rupture at the S–acyl bond. Thus on heating thianaphthenquinones, containing various substituents in the ring, with alcohols in the presence of chloramine-T, the disulphides related to the corresponding thiols were obtained[86]:



where R = CH_3, C_2H_5, and C_3H_7. A more highly oxidised compound (XX) is obtained as a side-product:

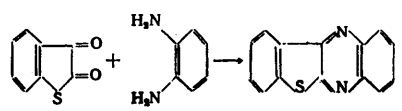


In the presence of sodium methoxide the β-phenylhydrazone of thianaphthenquinone is also split by methanol at the S–acyl bond; after treatment with methyl iodide, the phenyl hydrazone of methyl *o*-methylthiophenylglyoxylate was isolated[85]:

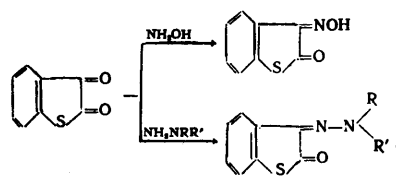


The aminolysis of thianaphthenquinone has not been studied.

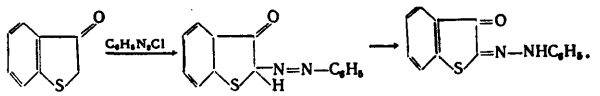
o-Phenylenediamine does not split the thiolactone ring the quinoxaline derivative of thianaphthenquinone being formed[82]:



The usual carbonyl reagents give derivatives of the β-carbonyl group of thianaphthenquinone only:



The corresponding derivatives of the α-carbonyl group can be obtained only by indirect pathways from thioindoxyl[85] (see p. 502), for example:

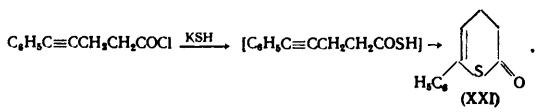


Thianaphthenquinone readily reacts with compounds containing an active methylene group[65,87,88], the reaction involving an α- or β-carbonyl group of thianaphthenquinone[89,90].

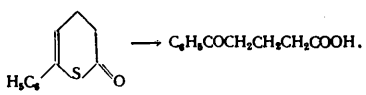
3. UNSATURATED δ-THIOLACTONES AND δ-THIOLACTONES CONDENSED WITH A BENZENE RING

Unsaturated δ-Thiolactones

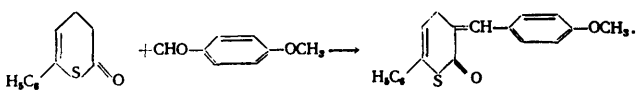
δ-Phenyl-δ-valerothiolactone (XXI) with a double bond in the γδ-position was obtained by the reaction of the chloride of 4-phenylbut-3-ynecarboxylic acid with potassium hydrogen sulphide. Evidently, 4-phenylbut-3-ynecarbothiolic acid is formed as an intermediate[60]:



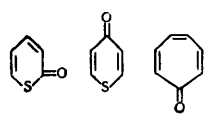
It is interesting that under the same conditions the unsaturated γ-thiolactone is formed from the chloride of the unsubstituted but-3-ynecarboxylic acid[60] (see p. 498). The structure of δ-phenyl-δ-valerothiolactone (XXI) was confirmed by its hydrolysis with 50% sulphuric acid to γ-benzoylbutyric acid:



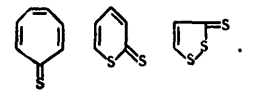
The condensation of δ-phenyl-δ-valerothiolactone with anisaldehyde has been described:



When a second double bond is introduced into the ring of an unsaturated δ-thiolactone, its thiolactone properties recede into the background, those associated with the conjugation of the free electron pair of the sulphur atom with the π electrons of the double bond coming to the fore. Thus the physical and chemical properties of α-thiopyrone resemble those of the isomeric γ-thiopyrone:

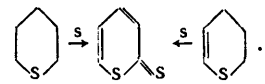


The distribution of electrons in α- and γ-thiopyrones is similar to that in tropone. These three isoelectronic compounds should have similar physical properties, which is usually found to be the case when the –CH=CH– group is replaced by –S–. Quantum-mechanical calculations and investigation of the chemical properties of α-thiopyrone confirmed that it is a pseudotropone. The above considerations apply also to α-dithiopyrone which should occupy an intermediate position between the hypothetical tropothione and "trithione", which exhibit aromatic properties.

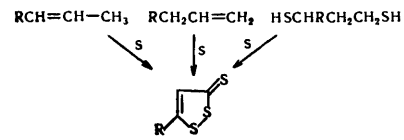


The investigation of α-thio- and α-dithio-pyrones was begun recently by Mayer and coworkers. The available data suggest that these compounds are aromatic.

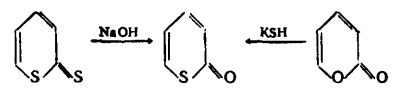
α-Dithiopyrone was obtained by the reaction of thiacyclohexane or thiacyclohexene with sulphur at a high temperature (about 200°)[91-93]:



This method resembles those for the preparation of "trithiones", by the reaction of certain olefins and mercaptans with sulphur under severe conditions[94,95]:



α-Dithiopyrone was also obtained from α-pyrone by successive treatment with phosphorus pentasulphide and sodium hydrogen sulphide[93]. Treatment of α-dithiopyrone with alkali leads to α-thiopyrone[93], which was also obtained by the reaction of α-pyrone with potassium hydrogen sulphide[96]:



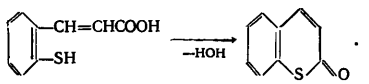
The aromatic character of α-thio- and α-dithio-pyrones is indicated primarily by their unusual thermal stability. When α-thiopyrone is brominated, substitution and not addition takes place[92].

α-Thiopyrone is soluble in water, which means that it is a polar compound. Since it is a pseudotropone, its physical and chemical properties are best represented by the formula:

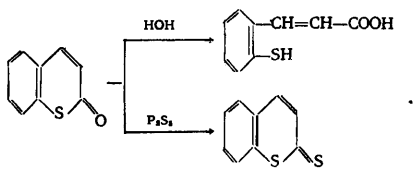
However, α-thiopyrone cannot be oxidised to the corresponding pseudotropolone, because the attack of oxidising agents is directed primarily to the divalent sulphur. On formation of the sulphone, the free electron pair of the sulphur atom is removed from the conjugation with the ring, as a result of which the compound loses its aromatic character[97].

Unsaturated δ-Thiolactones Condensed with a Benzene Ring

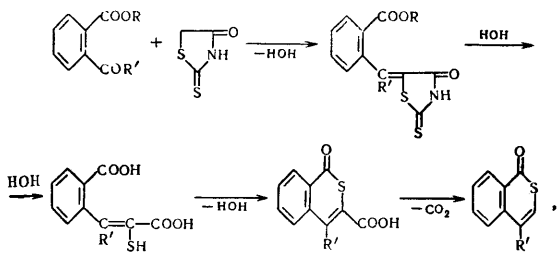
These compounds are not aromatic. One of such thiolactones, thiocoumarin, is formed on lactonisation of *o*-mercaptocinnamic acid[98]:



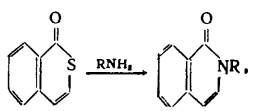
The *cis*-acid lactonises spontaneously, but the lactonisation of the *trans*-acid requires heating with dehydrating agents. The preparation of thiocoumarin from coumarin on heating with various derivatives of thiocarbonic acid [CS_2, $CS(NH_2)_2$, etc.] has been described[15]. Alkaline hydrolysis of thiocoumarin yields *cis*-*o*-mercaptocinnamic acid[98], and its reaction with phosphorus pentasulphide gives dithiocoumarin[99]:



The δ-thiolactone isomer of thiocoumarin (1,2-dihydro--1-oxo-2-thianaphthalene) is formed on alkaline hydrolysis of the products of the condensation of *o*-acylbenzoic acid or its esters with rhodanine[100,101]:

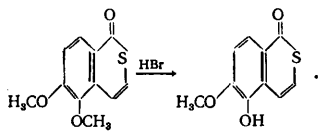


where R″ = H or CH_3. Ammonia and primary amines react with 1,2-dihydro-1-oxo-2-thianaphthalene with the formation of the corresponding isoquinoline derivative[101]:

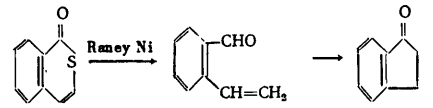


where R = H or alkyl. The mechanism of this reaction has not been studied.

1,2-Dihydro-5,6-dimethoxy-1-oxo-2-thianaphthalene dissolves in alkali on heating, but the hydrolysis product has not been investigated. Boiling hydrobromic acid does not affect the ring, causing only the demethylation of the 5-methoxy-group[101]:

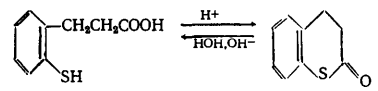


Elimination of sulphur from 1,2-dihydro-1-oxo-2-thianaphthalene with Raney nickel yields 1-indanone with the intermediate formation of *o*-formylstyrene[102], which is known to isomerise to 1-indanone:

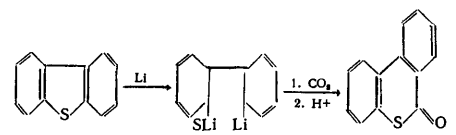


Saturated δ-Thiolactones Condensed with Benzene Rings

Lactonisation of *o*-mercaptohydrocinnamic acid gave dihydrothiocoumarin, which on alkaline hydrolysis was reconverted into the initial acid[98]:



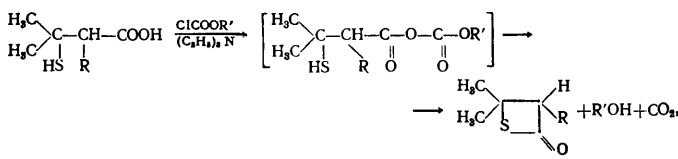
3,4-Benzothiocoumarin, a δ-thiolactone condensed with two benzene rings, was obtained by splitting dibenzothiophen with lithium and subsequent carboxylation[103]:



3,4-Benzocoumarin is obtained from dibenzofuran under the same conditions.

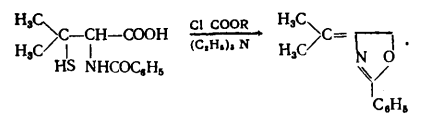
4. β-THIOLACTONES

β-Thiolactones have been less thoroughly investigated than γ- and δ-thiolactones. Attempts to prepare four--membered thiolactones were made in 1948 by Süs[104], but the first representatives of the class of β-thiolactones were actually obtained by Knunyants and coworkers in 1955[105,106] by the anhydridisation of β-mercapto-acids with chloroformic ester in the presence of triethylamine:



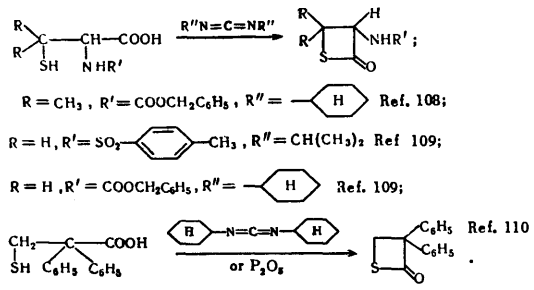
where R = H, $NHCOCH_3$, $NHCOCH_2C_6H_5$, or $NHCOCH_2$. .$NHCOCH_2C_6H_5$.

Anhydride formation from *N*-benzoyl-ββ-dimethylcysteine gave an unsaturated oxazolone:



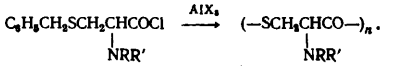
However, in the case of other α-acylamino-β-mercapto--acids the formation of oxazolone, even as a side-product, is not observed, the sole reaction products being β-thiolactones, as mentioned above. Thus anhydride formation from *N*-acyl-ββ-dimethylcysteine derivatives with chloroformic ester does not as a rule give the five-membered ring of oxazolone, the four-membered ring of β-thiolactone being formed[106,107].

Carbodiimides and phosphorus pentoxide can also be used as dehydrating agents in the preparation of β-thiolactones from β-mercapto-acids:

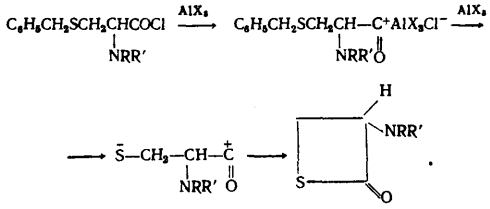


The dehydration of β-hydroxy-acids does not as a rule yield β-lactones.

Fleš and coworkers [47,111] obtained α-acylamino-β-propiothiolactones from the acid chlorides of *N*-acyl-*S*-benzylcysteine derivatives by the action of aluminium chloride or bromide. This method is similar to that used for the preparation of thio-oxindole from *o*-methylthiophenylacetyl chloride (p. 500), and its application is restricted to β-thiolactones which do not contain substituents sensitive to the action of aluminium chloride and the hydrogen chloride liberated during the reaction. The preparation of β-thiolactones by Fleš' method requires two moles of aluminium halide per mole of the initial acid chloride. When the acid chloride of an *N*-acyl-*S*-benzylcysteine derivative is acted upon by one mole of AlX_3, a linear polythioester is formed:

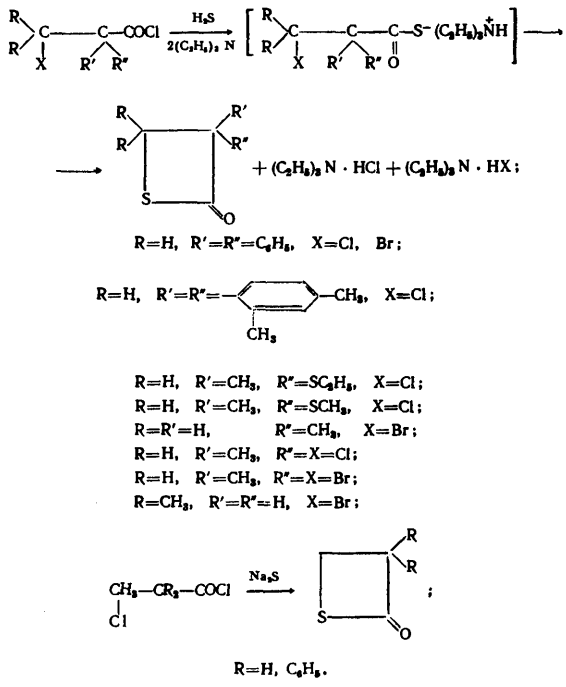


Ingold proposed the following mechanism to account for the different behaviour of the acid chlorides of *N*-acyl-*S*-benzylcysteine derivatives in the presence of one and two moles of aluminium halide [47]:



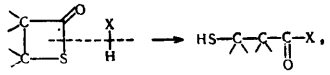
The first mole of AlX_3 ionises the covalent bond between the chlorine and the acyl group. Because of steric hindrance, the resulting cation is incapable of undergoing intramolecular debenzylation, but it can debenzylate another similar cation or molecule, which results in the formation of a polythioester. The second mole of AlX_3 debenzylates the acylium cation with the formation of a betain structure in which the reaction centres with opposed charges readily approach each other and the four-membered ring of β-thiolactone is formed.

The simplest and most convenient method for the preparation of β-thiolactones consists in the reaction between the acid chlorides of β-halogenocarboxylic acids with hydrogen sulphide in the presence of triethylamine [110] or a metal sulphide [30,31,110]:



The yields of β-thiolactones are related to their stability, which depends on the nature of the substituents. As in the case of γ- and δ-thiolactones, the stability of the β-thiolactone ring increases with the number of substituents.

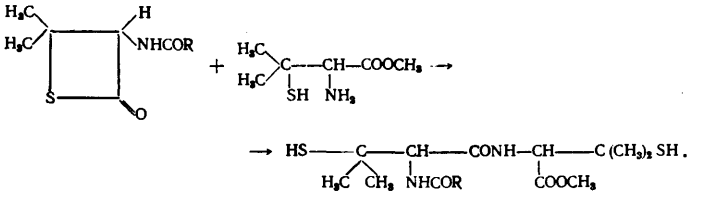
β-Thiolactones readily react with various nucleophilic reagents, the β-thiolactone ring always being ruptured at the S–acyl bond:



where X = OH, OR, or NRR'.

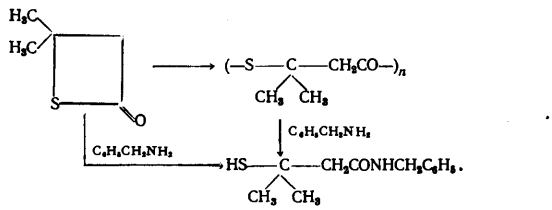
The hydrolysis of β-thiolactones in the presence of acids and alkalis leads to β-mercapto-acids, while their alcoholysis in the presence of acids or alkoxides gives esters of β-mercapto-acids. Ammonia [112] and aromatic [105,106,113] and aliphatic [105,112,113] amines split β-thiolactones with the formation of β-mercapto-acid amides.

The splitting of α-acylamino-β-thiolactones with α-amino-acids [113], their salts [105,112], and esters [114] can be used for the synthesis of peptides, for example:

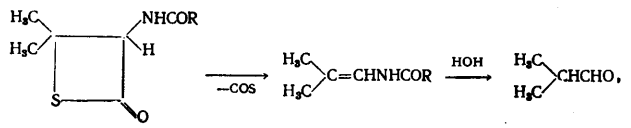


Knunyants and coworkers [114] were the first to achieve peptide synthesis using β-thiolactones. Later, this method was employed by Sheehan [108] and Fleš [109,111], and other workers extended it to γ-thiolactones (see p. 496).

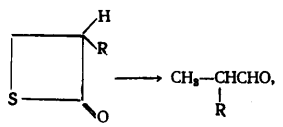
β-Thiolactones readily polymerise [105,111,113], the resulting polythioesters behaving as acylating agents [111,115], like the cyclic monomers, for example:



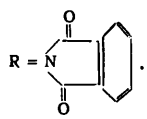
Other reactions which have been described, in addition to those between β-thiolactones with nucleophilic reagents and polymerisation, are pyrolysis of α-phenylaceturoylamino-ββ-dimethyl-β-propiothiolactone with elimination of carbon oxysulphide [106]:



where R = $CH_2NHCOCH_2C_6H_5$, and the reductive elimination of sulphur from α-phthalimido-β-propiothiolactone with Raney nickel [47]:



where

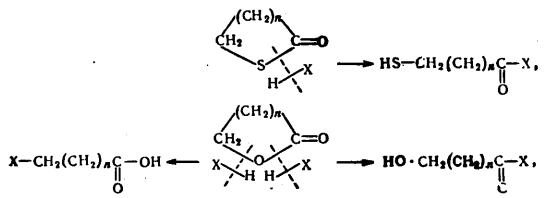


Treatment of α-benzyloxycarbonylamino-ββ-dimethyl--β-propiothiolactone with HBr in acetic acid did not result in ring opening. Under these conditions Sheehan [108] obtained the hydrobromide of α-amino-ββ-dimethyl-β-propiothiolactone.

β-Thiolactones are formed more readily and undergo ring rupture with greater difficulty than their oxygen analogues — β-lactones. This distinguishes β-thiolactones from γ- and δ-thiolactones, which are formed with greater difficulty and undergo ring rupture more readily than γ- and δ-lactones. The esters of carbothiolic acids are also less readily obtainable and more reactive than their oxygen analogues — carboxylic acid esters. Thus among the compounds with the $-\overset{\overset{O}{\|}}{C}-S-$ grouping only β-thiolactones are more stable than their oxygen analogue with the grouping $-\overset{\overset{O}{\|}}{C}-O-$. Apparently, this is due to the β-thiolactone ring being less strained than that of β-lactone, because the valence angle of sulphur is close to 90°¶. In γ- and δ-thiolactones and thiolic acid esters the decisive factor is the lower stability of the $\gtrless C-S$ bond compared with $\gtrless C-O$.

¶ From spectroscopic data, Fleš [111] confirmed that the four-membered ring in β-thiolactones is less strained than in β-lactones.

Thiolactones with rings of different sizes differ from the corresponding lactones not only in the stability of the ring but also in the nature of their reactivity. β-, γ-, and δ-thiolactones are split by nucleophilic reagents only at the S-acyl bond, whereas their oxygen analogues are split by the same agents at either the O-acyl or O-alkyl bonds.



where n = 1, 2, or 3.

Thus thiolactones behave only as acylating agents, in contrast to lactones which have both acylating and alkylating activity. The esters of carbothiolic acids are also more active acylating agents than carboxylic acid esters.

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THE CHEMISTRY OF 1,3,4-OXADIAZOLE DERIVATIVES

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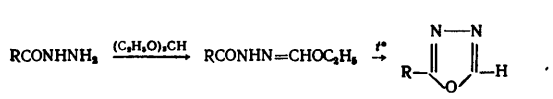
I. INTRODUCTION

There is now much experimental material on the chemistry of 1,3,4-oxadiazole derivatives, which are widely used in pharmacy, dyestuff production, scintillation technology, for the production of thermostable polymers, and in other fields of science and technology.

2,5-Substituted 1,3,4-oxadiazoles had been prepared before the end of the last century, but there have been no reviews on this subject; this article attempts to fill this gap, embracing the literature up to 1961, and including nearly all the most important material on the preparation and chemical properties of 2,5-substituted 1,3,4-oxadiazoles.

II. PREPARATION OF MONO-SUBSTITUTED 1,3,4-OXADIAZOLES

2-Aryl-1,3,4-oxadiazoles are prepared by the reaction of carboxylic acid hydrazides with excess of triethoxymethane [1-4]:

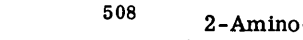


(I) (II)

The reaction is carried out at the boiling point of the triethoxymethane; the time of heating can be restricted to that necessary for complete dissolution of the hydrazide in the latter, which is usually several hours [2]. The amount of triethoxymethane can be as little as three moles per mole of hydrazide. At a lower temperature, compound (I) is formed in quantitative yield [1,3]; further heating converts this into compound (II). The method is a general one only when any functional substituents in the initial hydrazides are inert to the "ortho-ester".

In some cases 2-aryl-1,3,4-oxadiazoles can be obtained by conversion of functional groups in a previously prepared oxadiazole; for example, 2-(4-aminophenyl)-1,3,4-oxadiazole has been prepared by reduction of the (nitrophenyl)-oxadiazole with phenylhydrazine [2]. Reduction by agents which act in acid or alkaline media is inapplicable, because of the ready hydrolysis of the resulting oxadiazole under such conditions [2].

2-Amino-1,3,4-oxadiazole (III) is obtained by the removal of hydrogen sulphide from formyl thiosemicarbazide by means of lead oxide in ethanol [5,6]:

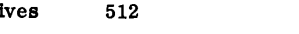


A considerable quantity of 3-mercapto-1,2,4-triazole is also produced.

III. PREPARATION OF SYMMETRICAL 2,5-SUBSTITUTED 1,3,4-OXADIAZOLES

1. 2,5-Dialkyl-1,3,4-oxadiazoles

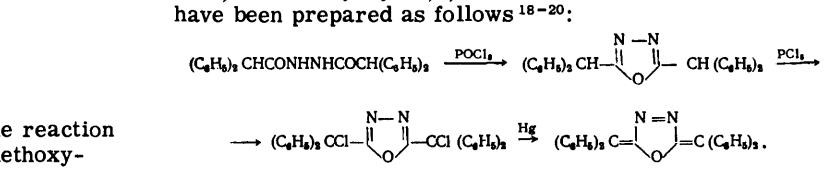
Symmetrical 2,5-dialkyl-1,3,4-oxadiazoles (IV) are prepared [7-14] by the reactions



where R = alkyl.

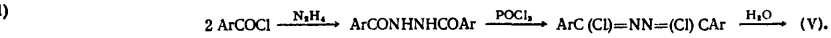
Aliphatic acids react readily with hydrazine hydrate at room temperature, giving a quantitative yield [15] of the symmetrical 1,2-diacylhydrazines, which are cyclised to the corresponding oxadiazoles either by heating in a vacuum [9-11] or by the action of phosphorus pentoxide [7,9], zinc chloride [7,12,15], phosphorus pentachloride or phosphoryl chloride [16] in benzene, thionyl chloride [14], or the anhydride of the corresponding aliphatic acid [8,9,12,13]. 2,5-Dialkyl-1,3,4-oxadiazoles are also formed by prolonged heating of esters of the aliphatic acids with hydrazine hydrate at 150–230° [9,12] or by heating the corresponding tetraacylhydrazines at 300–350°:

2,5-Dibenzhydryl-1,3,4-oxadiazole and its derivatives have been prepared as follows [18-20]:



2. 2,5-Diaryl-1,3,4-oxadiazoles

These compounds (V) are usually prepared as follows [21,22]:



The preparation of the 1,2-diaroylhydrazine from the aromatic acid chloride and hydrazine hydrate is conveniently conducted in dry pyridine, which combines with the hydrogen chloride liberated in the reaction, so avoiding the

need for excess of hydrazine hydrate [23] or for carrying out the reaction in aqueous alkaline solution [24]. In the production of the oxadiazole there is no need for prolonged boiling of the diaroylhydrazine with the phosphoryl chloride, as is sometimes recommended [21]; it is quite sufficient to heat till the starting material is completely dissolved.

Symmetrical 2,5-diaryl-1,3,4-oxadiazoles are also obtained directly from the corresponding diaroylhydrazines by heating at 180–350° [7,9,15,17,25-29] or by the action of phosphorus pentoxide [19,26-32], thionyl chloride [19,28] or oxalyl chloride [33]. The reaction product of the hydrazide with chlorinating agents can be cyclised to the oxadiazole by means of silver nitrate [28,34-37]. 2,5-Diaryl-1,3,4-oxadiazoles are also produced by heating mono- or tri-acylhydrazines [17,25,38]:

$$2\,ArCONHNH_2 \xrightarrow{\Delta} (V) + N_2H_4 + H_2O,$$

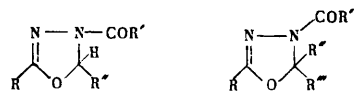
$$ArCONHN(COAr)_2 \xrightarrow{\Delta} (V) + ArCOOH;$$

by heating the silver salts of 1,2-diaroylhydrazines [39], by the action of iodine on the silver or mercury salts of the acylhydrazones (VI) [40]:

$$\underset{(VI)}{ArCONHN{=}CHAr} \xrightarrow{Ag} ArC(OAg){=}N{-}N{=}CHAr \xrightarrow{I_2} ArC(OI){=}N{-}N{=}CHAr \rightarrow (V),$$

and also, from the hydrazones (VI), by heating [40], by chlorination in carbon tetrachloride [41], or by boiling with a dilute alkaline solution of potassium cyanoferrate(III) or with isopentyl nitrite [40].

The action of acid chlorides on silver salts of the hydrazones (VI) produces dihydrooxadiazoles of type:

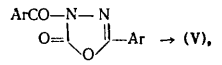


Of interest also is the preparation of aryl 1,3,4-oxadiazoles by the reaction of carboxylic acid monoacylhydrazides with iminium-ether chlorides at 80–160° [42] or by treatment of their reaction product with nitrous acid [43-46]:

$$ArC(=NH)NHNHCOAr \rightleftarrows ArC(NH_2){=}N{-}N{=}C(OH)Ar \xrightarrow{HNO_2}$$

$$\xrightarrow{HNO_2} ArC(OH){=}N{-}N{=}C(OH)Ar \rightarrow (V).$$

2,5-Diaryl-1,3,4-oxadiazoles have also been obtained by the decomposition of substituted 1,3,4-oxadiazol-5-ones at 280° [47,48]:



and by the hydrolysis of 3,6-diaryl-1,2-dihydro-1,2,4,5-tetrazines in the presence of mineral acids or alkalis [44,47-49].

IV. PREPARATION OF ASYMMETRICAL 2,5-SUBSTITUTED 1,3,4-OXADIAZOLES

1. 2-Alkyl-5-aryl-1,3,4-oxadiazoles

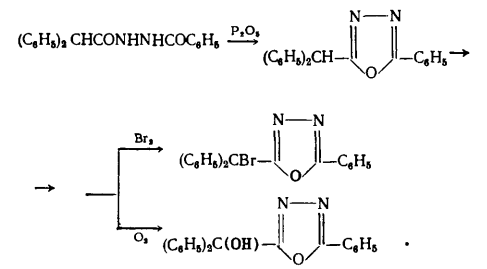
These compounds (VII) are obtained as follows [50]:

The aliphatic acid hydrazides are produced from the esters and hydrazine hydrate in a satisfactory yield at room temperature; under other conditions the hydrazides are readily converted into symmetrical 1,2-diacylhydrazines [51]. The kinetics of benzoylation of aliphatic hydrazides shows that the 1,2-diacylhydrazines are obtained in quantitative yield in dilute solutions at room temperature [51]. Cyclisation of the diacylhydrazines into oxadiazoles is carried out as described in Section III.

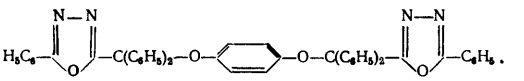
2-Alkyl-5-aryl-1,3,4-oxadiazoles can be prepared from hydrazides and "acid ortho-esters" [1] under conditions analogous to those used for 2-aryl-1,3,4-oxadiazoles (see Section II):

$$ArCONHNH_2 \xrightarrow{(C_2H_5O)_3CR} ArCONHN{=}CROC_2H_5 \xrightarrow{\Delta} (VII).$$

An interesting method is the preparation of oxadiazole derivatives from diphenylmethyl derivatives of 2-phenyl-1,3,4-oxadiazole, which are obtained by heating *N*-benzoyl-*N'*-diphenylacetylhydrazine with phosphorus pentoxide [52]:



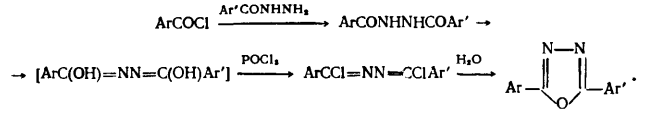
The bromine atom of the 5-(bromodiphenylmethyl)-2-phenyl-1,3,4-oxadiazole is replaced by the hydroxy-group by heating with aqueous alkali or by the ethoxy-group by reaction with sodium ethoxide [19,53]. Shaking with mercury in benzene in an atmosphere of carbon dioxide produces 9,9'-bis-(5-phenyl-1,3,4-oxadiazol-2-yl)-9,9'-bifluorenyl; in the presence of oxygen the product is bis[diphenyl-(5-phenyl-1,3,4-oxadiazol-2-yl)methyl] peroxide [53], which on dissolving in sulphuric acid decomposes to give 5-benzoyl-2-phenyl-1,3,4-oxadiazole [54]. Heating 5-(bromodiphenylmethyl)-2-phenyl-1,3,4-oxadiazole with mercury in the presence of *p*-quinone gives the ether [52]:



2-Alkoxy-5-aryl-1,3,4-oxadiazoles are also obtained by direct alkylation of oxadiazolones [55,56].

2. 2,5-Diaryl-1,3,4-oxadiazoles

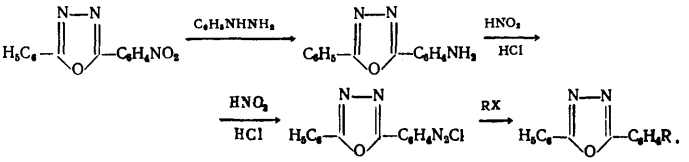
These compounds are generally prepared as follows [51,57]:



Most of the mixed aryl 1,3,4-oxadiazoles have been prepared by this method [21,50,58,59], and also uni- and bi-functionally substituted 2,5-diphenyl-1,3,4-oxadiazoles [21,57,60], the reaction conditions and yields being substantially independent of the position and type of substituent. Contrary to literature data, the diaroylhydrazines are formed in the

cold; elevated temperatures produce significant amounts of by-products, the symmetrical diaroylhydrazines of the type $(C_6H_5CONH)_2$ and $(XC_6H_4CONH)_2$, particularly when the benzene ring contains electron-accepting substituents. At the cyclisation stage, the period of heating the diaroylhydrazine with phosphoryl chloride can be restricted to the time necessary for its complete dissolution, instead of the boiling for several hours recommended in the literature [21].

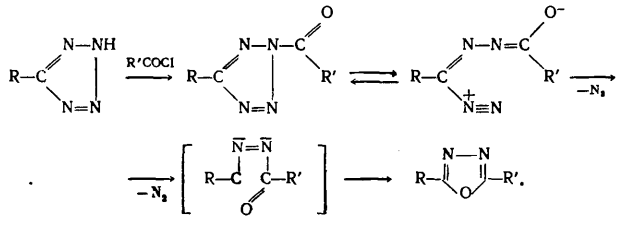
This method may be hindered by reaction of functional groups with the reagents used; the following procedure was devised to circumvent this [61]:



The 5-(aminophenyl)-2-phenyl-1,3,4-oxadiazoles are obtained in good yield using phenylhydrazine as reducing agent [57,61]. This method has been used for the partial reduction of dinitrophenyl-1,3,4-oxadiazoles in 1-methylnaphthalene as solvent, one of the nitro-groups in 2,5-di-(*p*-nitrophenyl)- and 2,5-di-(*m*-nitrophenyl)-1,3,4-oxadiazole being reduced fairly readily. In 2,5-di-(*o*-nitrophenyl)-1,3,4-oxadiazole, however, both nitro-groups are reduced simultaneously.

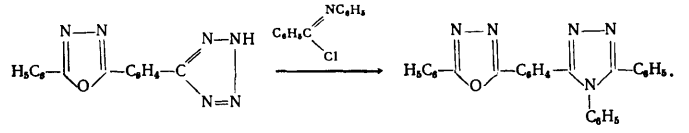
The nitro-group is also readily reduced to the amino-group if the 2,5-diphenyl-1,3,4-oxadiazole contains other substituents in addition, or if a phenyl ring is replaced by pyridyl, *e.g.* in the formation of 2-(*p*-aminophenyl)-5-(β-pyridyl)-1,3,4-oxadiazole. However, the presence of a heterocyclic residue makes amino-substituted 1,3,4-oxadiazoles considerably more difficult to obtain, because of their substantially lower chemical stability and the difficulty of isolating them from the reaction mixture. The amino-group in 1,3,4-oxadiazoles participates in all reactions appropriate to a primary aromatic amino-group [57], so that a whole series of substituted 1,3,4-oxadiazoles were able to be obtained, the chemical structures of which were fully confirmed by other methods of preparation.

Asymmetrical 2,5-diaryl-1,3,4-oxadiazoles can be obtained in good yield by heating 5-substituted tetrazoles with carboxylic acid chlorides in pyridine; the following has been suggested [62] as the reaction mechanism:



Acid anhydrides are also used as acylating agents.

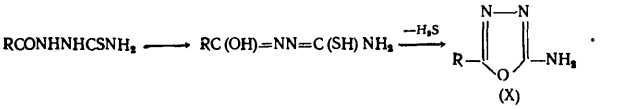
The action of imidoyl chlorides on compound (VIII) produces compound (IX), in which an oxadiazole ring and a triazole ring are joined by a benzene ring [63]:



(VIII) (IX)

3. Derivatives of 2-Amino-1,3,4-oxadiazole

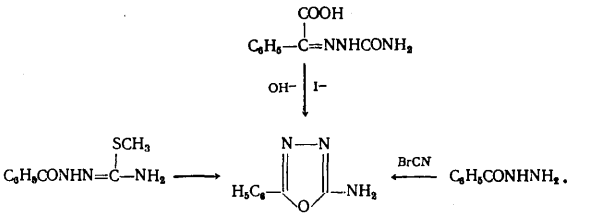
2-Amino-1,3,4-oxadiazole (X) and its derivatives are obtained by the elimination of hydrogen sulphide from thiosemicarbazides by means of lead monoxide [5,6,64]:



(X)

Good yields are obtained by heating a solution of the thiosemicarbazide in 95% ethanol with a tenfold excess of lead monoxide for several hours [5,6,64].

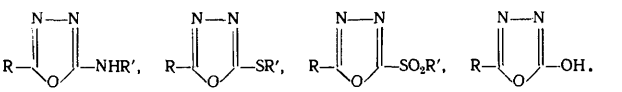
2-Amino-5-phenyl-1,3,4-oxadiazole has been prepared by the following routes [65]:



Heating the thiosemicarbazide derivatives

$$RCONHNHCSNHR' \text{ and } RCONHN{=}C(SCH_3)NHR',$$

or the action of dehydrating agents on them, has given the corresponding oxadiazoles [66-68]:

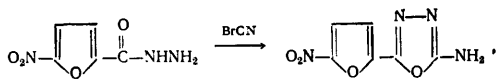


The action of a 5% sodium hypobromite solution on benzaldehyde semicarbazone produces 2-amino-5-phenyl-1,3,4-oxadiazole [69]. A number of other derivatives of 2-amino-5-phenyl-1,3,4-oxadiazole have also been prepared [70-77].

4. Heterocyclic 2,5-Substituted 1,3,4-Oxadiazoles

1,3,4-Oxadiazoles containing various heterocyclic substituents have been prepared analogously to the 2,5-diaryl-1,3,4-oxadiazoles [78-81]. The preparation of the heterocyclic acid acylhydrazides from the acid chlorides and the hydrazides must be carried out in the cold, since the use of elevated temperature gives, in addition to the main reaction product, the diacylated hydrazides $RCONHN(COR)_2$, which on hydrolysis gives the original monoacylhydrazide. In the preparation of aroylhydrazides in boiling solutions, symmetrical 1,2-diaroylhydrazines are also obtained, in addition to the other products specified [82]. The usual solvent for the production of acylhydrazides is pyridine, which binds the hydrogen chloride liberated in the reaction, and thus favours more complete utilisation of the initial reactants and, in the case of pyridinecarboxylic acid acylhydrazides, the production of the product as the free base. However, the extraction of the acylhydrazides from the reaction mixture is more difficult, because of their good solubility in pyridine [82].

Of interest is the preparation of heterocyclic derivatives of 2-amino-1,3,4-oxadiazole from cyanogen bromide and the heterocyclic acid hydrazide [56]:



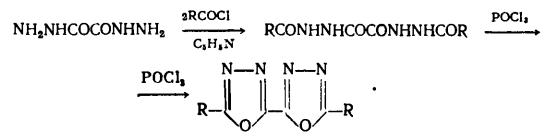
or by reaction of the heterocyclic acid chloride with thiosemicarbazide with subsequent cyclisation to the oxadiazole [56].

A number of heterocyclic derivatives of 1,3,4-oxadiazole have been prepared by these methods [1,40,83-88].

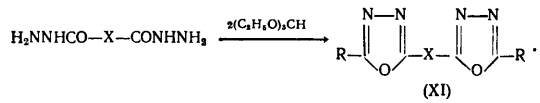
V. PREPARATION OF POLY-1,3,4-OXADIAZOLES

1. Bis-1,3,4-oxadiazolyl Derivatives

Bi-(1,3,4-oxadiazolyl)s are obtained by the general method for 2,5-substituted 1,3,4-oxadiazoles [21,89]:



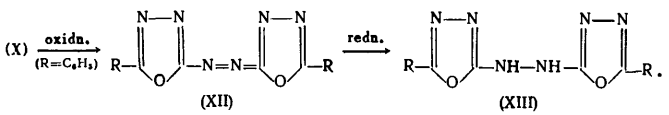
The same method is applied to bis-(1,3,4-oxadiazolyl) derivatives in which the oxadiazole rings are separated by hydrocarbon chains, by using the hydrazide of the appropriate dicarboxylic acid. In many cases the production of the secondary dihydrazide from the primary dihydrazide and the appropriate acid chloride in pyridine also gives significant amounts of a substance corresponding in properties and analysis to the diaroylhydrazine, and which with phosphoryl chloride produces the 2,5-disubstituted 1,3,4-oxadiazole. Bis-(1,3,4-oxadiazolyl) compounds of type (XI) in which R = H have been prepared by the action of triethoxymethane on the primary dihydrazide followed by cyclisation [1,89]:



(XI)

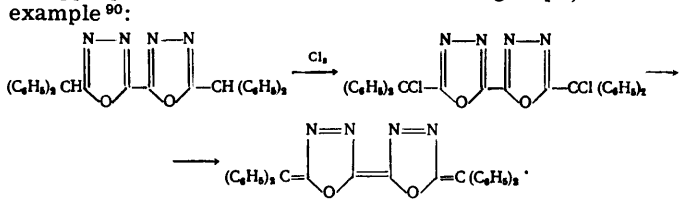
The action of triethoxymethane on malonodihydrazide gives a derivative of bis-(1,3,4-oxadiazolyl)methane in which the hydrogen atoms of the methylene group have been replaced by the group $=CH-OC_2H_5$.

Oxidation of 2-amino-1,3,4-oxadiazole derivatives gives azooxadiazoles (XII), which can be reduced to the corresponding hydrazo-compounds (XIII) [5]:

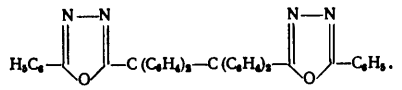


(XII) (XIII)

Other bis-(1,3,4-oxadiazolyl) compounds can be obtained by appropriate conversions of functional groups, for example [90]:



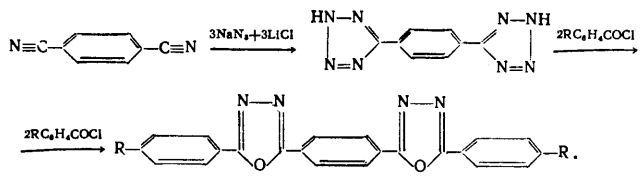
Bis-(1,3,4-oxadiazole) compounds such as the following have also been prepared [20,52]:



Other methods can also be used to obtain bisoxadiazole compounds [30,40,91].

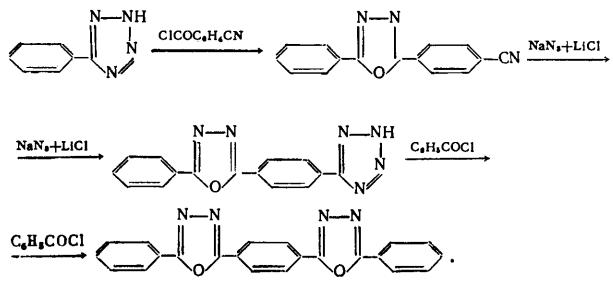
2. Poly-1,3,4-oxadiazole Derivatives

The thermal decomposition of 5-substituted 2-acyltetrazoles at 60–120° produces 1,3,4-oxadiazoles [62]. This is the basis of a procedure for the preparation of polyaryls containing up to nine rings in the molecule by reacting 5-phenyltetrazole or 1,2-di(tetrazol-5-yl)benzene with acid chlorides RC_6H_4COCl, where R = H, *p*-NO_2, or *p*-CN, [92] *e.g.*

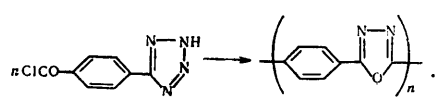


The terminal nitrile groups of the reaction product of *p*-cyanobenzoyl chloride with 1,4-di(tetrazol-5-yl)benzene can again be reacted with lithium azide in boiling dimethylformamide to produce tetrazole rings, which in their turn can be reacted with the acid chlorides, etc., so increasing the number of oxadiazole rings in the chain.

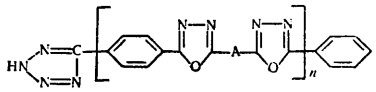
Polyoxadiazoles can also be obtained from 5-phenyltetrazole and *p*-cyanobenzoyl chloride [92]:



Polymers with an even number of aromatic rings can be prepared from 4-(tetrazol-5-yl)benzoyl chloride, which contains both the functions necessary for forming the oxadiazole ring [92]:



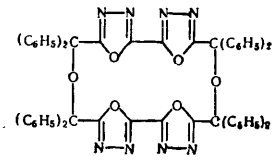
The action of dibasic acid chlorides on 1,4-di(tetrazol-5-yl)benzene gives the polymers [93]:



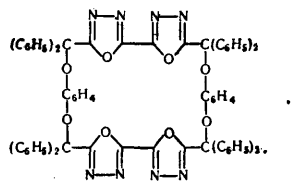
where n = 17–50.

The polyoxadiazoles are obtained in yields of up to 96%, and have a high melting point and a low solubility in organic solvents. It is thought that higher-molecular-weight polyoxadiazoles with alternating benzene and oxadiazole rings could be obtained by introducing a methyl or alkoxy-group. If pyridine nuclei are introduced between the oxadiazole rings the resulting polymers are black and are soluble in formic acid and phenol.

Cyclic polyoxadiazoles have also been prepared[20]:



and



VI. PROPERTIES AND USES OF 1,3,4-OXADIAZOLE DERIVATIVES

2,5-Substituted 1,3,4-oxadiazoles are colourless substances; the lower alkyl derivatives are liquids which distil without decomposition. Replacement of an alkyl residue by an aryl radical considerably raises the melting and boiling points. Usually the asymmetrical 1,3,4-oxadiazole derivatives melt and boil at lower temperatures than the symmetrical compounds. The presence of substituents of various electronic types on the aryl residues of the oxadiazoles leads to the appearance of colour in the compounds. Certain 2,5-substituted 1,3,4-oxadiazoles which have no strong electron-accepting groups luminesce in the crystalline state, in non-polar solvents or solvents of low polarity, and in polystyrene[81,94-97].

2-Hydroxy-5-aryl-1,3,4-oxadiazoles may exist in the keto-form[47,48,98-101].

Methylation of 2-amino-5-phenyl-1,3,4-oxadiazole with methyl iodide produces 2,3-dihydro-2-imino-3-methyl-5-phenyl-1,3,4-oxadiazole, while acetylation and nitrosation proceed normally; this shows that 2-amino-5-phenyl-1,3,4-oxadiazole can react either in the imino- or the amino-form[102].

The solubility of oxadiazoles in water varies with the substituents present[50]; thus while 2,5-dimethyl-1,3,4-oxadiazole is miscible with water in all proportions[7], the solubility of 2,5-diphenyl-1,3,4-oxadiazole in water is only 0.03%.

Aqueous solutions of mineral acids and alkalis cause rupture of the heterocyclic ring, with formation of the corresponding hydrazide. 2-Aryl-1,3,4-oxadiazoles hydrolyse almost instantaneously as soon as they are dissolved, giving the primary hydrazides and formic acid[2,5,7,10,103,104]. The tendency of oxadiazoles to hydrolyse decreases with their solubility[50].

Concentrated sulphuric acid (sp. gr. 1.84) does not sulphonate 2,5-diphenyl-1,3,4-oxadiazole even at 100° for 4 h or longer, but only produces the double sulphate, which hydrolyses readily in dilute aqueous solution to regenerate the initial 2,5-diphenyl-1,3,4-oxadiazole[105].

Concentrated nitric acid (sp. gr. 1.51) readily nitrates 2,5-diphenyl-1,3,4-oxadiazole to a mixture of the *o'o"*-, *m'm"*-, and *p'p"*-dinitro-compounds (in yield of 40, 20, and 27% respectively)[105].

A mixture of concentrated nitric and sulphuric acids nitrates 2,5-diphenyl-1,3,4-oxadiazole to 5-(*m*-nitrophenyl)-2-phenyl- and 2,5-di-(*m*-nitrophenyl)-1,3,4-oxadiazole in yields of 31 and 38%[105].

As has already been stated, a nitrophenyl group in a 1,3,4-oxadiazole is readily reduced to aminophenyl by phenylhydrazine. Reducing agents which require acidic or alkaline media (zinc dust, sodium disulphide) are unsuitable, since under such conditions the oxadiazole ring is attacked, producing first the corresponding hydrazide, and then hydrazine and aromatic acids[2,61].

The amino-group in an aminophenyl-1,3,4-oxadiazole can be diazotised and replaced by other substituents, for example halogens and the hydroxy- or cyano-groups, which in their turn can be used to provide further functionally substituted 1,3,4-oxadiazoles[57,61]. The diazotised amino-groups couple readily, producing azo-dyestuffs[106,107].

In dilute hydrochloric acid 2-amino-5-phenyl-1,3,4-oxadiazole reacts with nitrous acid to give 2-nitrosamino-5-phenyl-1,3,4-oxadiazole, which can be reduced to 2-hydrazino-5-phenyl-1,3,4-oxadiazole; this with nitrous acid produces 2-azido-5-phenyl-1,3,4-oxadiazole[5].

2-Hydrazino-5-phenyl-1,3,4-oxadiazole with benzaldehyde gives the corresponding substituted hydrazone, which is decomposed by hydrochloric acid and steam into benzaldehyde, benzoic acid, and $H_2NNHCONHNH_2$.[5]

Phenylhydrazinium chloride opens the oxadiazole ring of 2-amino-5-aryl-1,3,4-oxadiazoles, producing diaminoguanidine[108].

Heating 5-alkyl-2-amino-1,3,4-oxadiazoles with hydrazine hydrate gives 3-alkyl-4,5-diamino-1,2,4-triazoles in low yields[109].

Alkaline reactants convert 2-amino-5-phenyl-1,3,4-oxadiazole into 2-phenyl-1,3,4-triazol-5-one[65].

Raney nickel destroys the heterocyclic ring of 1,3,4-oxadiazoles, giving the corresponding amides[110].

Molecular bromine does not brominate 2,5-diphenyl-1,3,4-oxadiazole, but forms only complexes between the oxadiazole and the bromine[111]; a mixture of chlorine and iodine produces a complex of the 2,5-diphenyl-1,3,4-oxadiazole with iodine chloride[41]. In alcoholic solution 1,3,4-oxadiazoles also readily give complexes with $AgNO_3$ and $HgCl_2$.[7,9,15,28,29,112]

2-Substituted 1,3,4-oxadiazoles can be determined by potentiometric titration with sodium nitrite[103,104]; 2,5-diaryl-1,3,4-oxadiazoles can be analysed argentometrically[112].

Ultraviolet[81,95,97,113-118], infrared[92,119], luminescence[81,95-97,120], and Raman spectra[121] of 1,3,4-oxadiazole derivatives have been investigated. Dipole moments have been measured[122], the normal vibrational frequencies of the oxadiazole ring have been calculated[123], and polarographic studies have been made[124,125]. The scintillation efficiency of 1,3,4-oxadiazole derivatives has been determined in toluene[59,126-128] and polystyrene[94-96,129-131].

1,3,4-Oxadiazoles are widely used in pharmacy as anti-tubercular preparations[75,76,83-85], in the production of vat dyes[60,132-148] and azodyes[106,107,148], in colour photography[149-151], in scintillator technology[59,95,96,126,127,129-131], and for the production of thermostable polymers[92,93].

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THE FORMATION OF BIOCHEMICALLY IMPORTANT COMPOUNDS IN THE PRE-BIOLOGICAL STAGE OF THE EARTH'S DEVELOPMENT

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1. INTRODUCTION

The origin of life on Earth was preceded by a period of grandiose length, variously estimated at 1000–2500 million years, during which the compounds necessary for biological activity were formed. During this gigantic time interval, conditions were gradually created under which more and more complex compounds could be gradually formed from the simplest starting materials present on the Earth; these compounds included protein precursors, nucleic acids, lipids, etc., followed by more complex systems of these molecules directly leading to the appearance of life.

As recently as 10–15 years ago, the main stages of this gigantic pathway remained entirely obscure. At present our knowledge of conditions existing on the Earth in its primary evolutionary period has been greatly extended. This has led to attempts to set up models for the synthesis of various biochemically important compounds on the basis of starting materials that could exist on the primary Earth. The number of papers on this subject has now increased to the point where it has become necessary to summarise and analyse this problem, which is of great general scientific interest. The present review is intended to meet this need.

2. POSSIBLE CONDITIONS FOR PRIMARY SYNTHESES ON EARTH

It is now generally accepted that the Earth's primary atmosphere contained mainly H_2, CH_4, NH_3, and water vapour[1,2]. In the upper layers of the atmosphere photodissociation of water molecules could have been caused by short-wave solar radiation and this probably led to the formation of a certain amount of oxygen and carbon monoxide, but undoubtedly the atmosphere retained its reductive character. The loss of hydrogen from the atmosphere by diffusion into cosmic space might have been considerable even at that time; if the present concentration of molecular hydrogen in the atmosphere is $\sim 10^{-6}$ atm at the Earth's surface, the pressure in the primary atmosphere considered here may be taken as $\sim 1.5 \times 10^{-3}$ atm,[3] although at the very beginning of the Earth's formation it was considerably higher. The giant planets (Jupiter, Saturn, and those more remote) contain tremendous amounts of H_2, CH_4, and NH_3, even at the present time. Meteorites and comets formed an important source of primary materials on the Earth. It is estimated that in the first 2000 million years of the Earth's existence comets alone contributed up to 10^{12} tons of these compounds, or frozen radicals such as CN, CH_2, NH, NH_2, etc.[4] Reduced materials also predominate in the composition of meteorites; various hydrocarbons have been observed in stony meteorites (chondrites).

These compounds might have accumulated in the primary hydrosphere of the Earth, and surface rock decomposition products as well as products separated from the internal layers might also have been taken up; these products include H_2, CH_4, NH_3, CO, and H_2S,[5] also NH_4Cl, and later $Ca(NO_3)_2$;[6] Miller and Urey[3] discuss equilibrium between $CaCO_3$ and NH_3. Activation of these molecules by various forms of energy led to the formation of more complex compounds.

Solar radiation was undoubtedly the most powerful energy source; the total energy from this source reaching the Earth's surface is 1.2×10^{21} kcal per year. The solar radiation of photochemical importance was mainly the ultraviolet (below 400 mμm); relative to the Earth it amounted to $\sim 10^{20}$ kcal per year, and this reached the surface in the prebiological period of the Earth's existence[1]; according to Sagan[7], the flux of ultraviolet radiation in the 2400–2900 Å region that reached the Earth's surface amounted to $\sim 10^4$ erg cm^{-2} s^{-1}. Effective cleavage of CH_4 occurs at $\lambda < 1450$ Å, of H_2O at $\lambda < 1850$ Å, of NH_3 at $\lambda < 2250$ Å, and of CO at $\lambda < 1545$ Å.[3,8] Water molecules adsorbed on zinc oxide or silicates are decomposed by radiation of wavelength in the region 2300 Å, but when gaseous ammonia is adsorbed on active aluminium oxide, the photodissociation threshold of NH_3 shifts to 2700 Å.[8] The formation of formaldehyde has been noted[9,10] when a mixture of $NH_3 + CH_4 + H_2O$ is exposed to ultraviolet radiation in the 1450–1900 Å region, and also when a mixture of CH_4 and H_2O is irradiated. The presence of formaldehyde has also been demonstrated[11] in an irradiated mixture of $CO + H_2O$. The photoionisation of gases and vapours by ultraviolet radiation has been reviewed by Vilesov[12].

Electrical discharges in the atmosphere formed the next important energy source, but they were less important than ultraviolet radiation. It is estimated[1] that electrical discharges accounted for $\sim 1.2 \times 10^{15}$ kcal over the whole Earth's surface. According to Miller and Urey[3], ultraviolet radiation of wavelength $\lambda < 2500$ Å amounted to 660 cal cm^{-2} per year, whereas the energy from electrical discharges was only 4 cal cm^{-2} per year. However, it must be borne in mind that the action of electrical discharges was localised in relatively small spaces, but the action of ultraviolet light was uniformly spread in the atmosphere; moreover it is possible that under primary Earth conditions thunderstorm activity was more intense. When a discharge occurs in a mixture of $CH_4 + NH_3 + H_2O$ the compounds formed include aldehydes and HCN;[13,14] when H_2S is added thiourea and ammonium thiocyanate are also formed[14].

The action of cosmic rays and charged particles emitted by the Sun might have been of great importance. At present, most ionising particles of this kind are held by the Earth's magnetic field and deflected to form a radiation belt. The role of this factor is therefore estimated[3] at three orders lower than that of electrical discharges, but this might have been different in the early period of the Earth's development. According to Uffen[15], the formation of radiation belts as a result of movements in the Earth's crust occurred 2500 million years ago. Up to that time corpuscular

radiation[16,17] reached the Earth's surface and led to the activation of simple compounds. Calvin and coworkers[18] detected formaldehyde in aqueous solutions of CO_2 that had been irradiated in a cyclotron with a stream of helium particles, but the real significance of this reaction is insufficiently based on geochemical data. Subsequently, Calvin and coworkers[19,20] subjected a mixture of methane, ammonia, and water to the action of fast electrons (5 MeV) and showed that under these conditions HCN, urea, and other products are formed.

The action of all the types of radiation mentioned is based on the breaking of C–C, C–H, H–O, and other bonds and on the formation of a number of radicals: OH, H, CH_2, CN, NH, etc.

In contrast, the action of heat — the most substantial non-ionising factor — consists in the activation of molecules of primary compounds by exciting their vibrational levels. Thermal solar radiation is undoubtedly the most significant here; as already mentioned, this amounts to 10^{21} kcal per year over the whole of the Earth's surface; about half this quantity is reflected. Heat flux from the interior to the surface is another factor in the Earth's heat balance; this is largely of radiogenic origin (disintegration of ^{40}K, ^{235}U, etc.) and amounts to $\sim 10^{17}$–10^{18} kcal per year[21]. The temperature of the Earth's surface was, at any rate, less than 100°.[22] However, in the same way as the density of electrical discharges in the path of lightning was much greater than the average values given above, so also the distribution of temperature on the Earth's surface was heterogeneous with sharp maxima at the points where volcanoes and geysers erupted. Volcanic eruptions produced large amounts of incandescent gases such as H_2S and SO_2; moreover, the liberation of NH_4Cl and other ammonium compounds by volcanoes and fumaroles must be taken into account[6].

In general, it may be assumed that in the first period of the Earth's existence as a planet H_2, CH_4, NH_3, CO, H_2S, CH_2O, HCN, and NH_4Cl and other compounds were present; these compounds themselves had no biochemical significance but they were the starting materials for the formation of compounds that entered into the composition of living organisms. In this period the main sources of energy were various ionising radiations, primarily short ultraviolet radiation, and, to a lesser extent, electrical discharges and heavy ionising particles; the role of these particles must be considered of greater significance than previously. Of the non-ionising types of energy, the action of heat must be taken into account.

Therefore, after 2000–2500 million years, when the reductive atmosphere gave place to an oxidative atmosphere, a layer of oxygen retained ultraviolet radiation; the radiation belts that arose at this time deflected the main mass of ionising particles from the Earth, and volcanic and thunderstorm activity began to die down. In this relatively quiet background the formation and development of life became possible. However, it can easily be seen that in the very first period of the Earth's existence the compounds present and the radiation conditions excluded the possibility of life, but were favourable to the chemical evolution of substances needed for the formation of various compounds that enter into the composition of living organisms.

We shall now consider possible paths in the formation of the main classes of biochemically important compounds from the starting compounds mentioned above, bearing in mind the sequence of energy sources.

3. AMINO-ACIDS

The formation of amino-acids has attracted much attention, because of the great significance of these compounds in the subsequent synthesis of polypeptides and proteins, and because of the relative ease with which a number of amino-acids can be prepared from simple starting materials.

Groth[23,24] found that glycine and alanine were formed when ultraviolet rays in the region of 1470 and 1295 Å (resonance lines of xenon lamp) acted on a mixture of $CH_4 + NH_3 + H_2O$ for 24 h, and when methane was replaced by ethane, α-aminobutyric acid was also formed. Terenin[8] used a hydrogen lamp with a spectrum in the region $\lambda > 1300$ Å, which is closer to the short-wave radiation spectrum of the Sun. He irradiated a mixture of $CH_4 + NH_3 + CO$ in contact with liquid water and found alanine in the reaction products. Later, Dodonova and Sidorova[9], working in Terenin's laboratory, irradiated the same mixture with ultraviolet rays in the 1800–1450 Å region and found that glycine, alanine, α-aminobutyric acid, valine, and leucine (or norleucine) were formed. When H_2S or CS_2 was added to the gas mixture, no sulphur-containing amino-acids were found[25]. When methane was replaced by ethane[10] the composition of the amino-acids formed remained unchanged.

Pavlovskaya and Pasynskii[26] irradiated aqueous solutions containing 2.5% of CH_2O and 1–1.5% of NH_4NO_3 or NH_4Cl with ultraviolet light from a PRK-2 lamp (2.7×10^6 erg cm^{-2} min^{-1} at 40–45° for 20 h) and found that the following amino-acids were formed: serine, glycine, glutamic acid, alanine, valine, and also basic amino-acids; phenylalanine was found in small amounts in mixtures containing NH_4Cl at 40° and NH_4NO_3 at +1°. The reaction mixtures were analysed on columns and on paper, and a microphotometer was used to measure the chromatograms. In the presence of adsorbents (bentonite, kaolinite, limonite, and optical quartz)[27], the same amino-acids were found with the exception of basic amino-acids in some systems; moreover, the formation of isoleucine or phenylalanine (which have close R_f values) was also confirmed. In subsequent work[28] irradiation was carried out with a BUV-15 bactericidal lamp giving 80% of its radiation at 2537 Å; 1.5 litres of solution at 40° was irradiated for 20–40 h. The formation of amino-acids observed previously was confirmed and threonine was also found; phenylalanine and valine were not detected in these experiments. In some experiments formaldehyde was replaced by acetaldehyde and the resulting reaction mixtures showed the presence of arginine and tyrosine in addition to the acids previously mentioned; the presence of tyrosine confirms the formation of aromatic amino-acids. With the concentrations of starting materials mentioned above, the amino-acid content of the mixture after irradiation varied from 10^{-4} to 5×10^{-3} M, the lower figure referring to alanine. Thus, irradiation of a solution of simple starting materials leads to the formation of a number of important amino-acids.

Deschreider[29] showed that irradiation with ultraviolet rays of wavelength 2537 Å produced alanine, glycine, and aspartic acid, but the mixtures he used were too complex, maleic and succinic acid being used as starting materials. The work of Cultrera and Ferrari[30] suffers from the same disadvantage: they used dibasic acids, keto-acids, and hydroxycarboxylic acids as starting materials together with various nitrogenous compounds and their irradiation products included glycine, alanine, serine, and dicarboxylic amino-acids. Rid[31] demonstrated the formation of glycine,

but his irradiation mixture contained hydroxy-amines and CO_2. The work described in these three papers is therefore not fully justified by geochemical considerations.

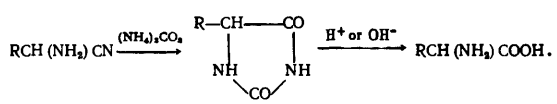
As early as 1913 Loeb[32] observed the formation of glycine when electrical discharged acted on a mixture of CO, NH_3, and H_2O, and also on 5–10% solutions of formamide. However, the most detailed work in this field is due to Miller[13,33,34], who found that glycine, alanine, aminodicarboxylic acids, aminobutyric acid, and sarcosine were formed in a continuously circulating mixture of $CH_4 + NH_3 + H_2 + H_2O$ subjected to spark and silent discharges for a week; the amino-acid concentration in the mixture was equivalent to 5×10^{-5}–5×10^{-3} M. It was shown that aldehydes (up to 10^{-3} M) and HCN (up to 4×10^{-2} M) are formed as intermediates; the kinetics of NH_3 loss, intermediate formation of HCN and aldehydes, and amino-acid accumulation were studied (Fig. 1).

Miller's results were confirmed by Pavlovskaya and Pasynskii[26], but they eliminated the excess of hydrogen in Miller's mixtures and replaced it by CO; this replacement was dictated by thermodynamic calculations. It was shown[26,34] that the irradiated solutions were sterile. With the spark discharge through the mixture for 100 h the formation of the same amino-acids was observed and HCN was found in the solution after the discharge.

The formation of the amino-acids appears to have been through a cyanhydrin stage by a mechanism closely related to that of the Strecker synthesis[35]. Strecker developed a method for preparing alanine from acetaldehyde by the following reaction:

$$RCHO + NH_3 \rightarrow RCH(NH_2)OH \xrightarrow{HCN} RCH(NH_2)CN \xrightarrow{2H_2O} RCH(NH_2)COOH.$$

This method was later used for the synthesis of various amino-acids (glycine, valine, phenylalanine, glutamic acid, etc.), but it was found most convenient for alanine, glycine, and serine. Bücherer[36] introduced an interesting modification in which an aminonitrile is heated with ammonium carbonate and the 5-hydantoin formed is hydrolysed:



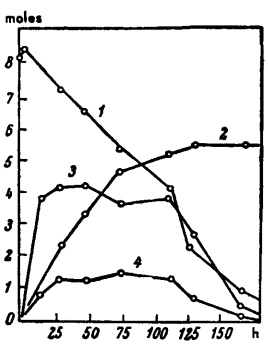


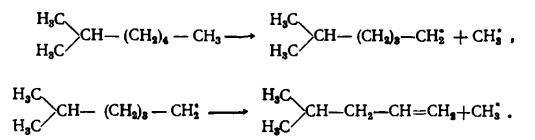
Fig. 1. Concentration of ammonia, hydrogen cyanide, aldehydes, and amino-acids during passage of a spark discharge through a mixture methane, ammonia, water, and hydrogen[13]: 1) NH_3 ($\times 100$); 2) amino-acids ($\times 10^3$); 3) HCN ($\times 10^2$); 4) aldehydes ($\times 10^3$).

Unfortunately, most other methods of synthesising amino-acids (with malonic ester, from keto-acids, etc.) are too complicated for the setting up of geochemical analogies. Here the Strecker synthesis has the undoubted advantage that it permits the assumption that any process that leads to the formation of aldehydes and HCN could have promoted the accumulation of α-amino-acids in the primary Earth's hydrosphere.

Abelson[37] who studied the action of a spark discharge on a mixture of various gases, found that NH_3 cannot be replaced by N_2; he also studied the effect of adding CO_2 and CO. He found that glycine, alanine, and sarcosine were formed. His results have been confirmed on mixtures corresponding in composition to those of Miller. That it was impossible to make do with $CO_2 + N_2$ has also been shown by Heyns and coworkers[14]; addition of H_2S to a reductive gas mixture yielded no sulphur-containing amino-acids. Frank[38] studied the action of a spark discharge on Miller's gas mixture, and also on a mixture in which $CH_4 + H_2$ was replaced by methanol and isooctane, but he could not extend the number of amino-acids formed. It appears that when an electrical discharge acts on hydrocarbon chains only small radicals are eliminated ($CH_3^{\cdot}$ type), as in the degradation of CH_4 and CH_3OH:

$$CH_4 \rightarrow CH_3^{\cdot} + H^{\cdot} \qquad (98.2 \text{ kcal}),$$

$$CH_3OH \rightarrow CH_3^{\cdot} + HO^{\cdot} \qquad (78.3 \text{ kcal}),$$



Oró[39] made a detailed study of the action of a spark discharge (spark length 1.5–3 cm) on conc. NH_4OH (15 M) at 30° for 5–7 h in an atmosphere of CH_4 and C_2H_6. ^{14}C-Hydrocarbons were used in some experiments and this enabled autoradiography to be used in the analysis of the two-dimensional chromatograms; the ultraviolet absorption of eluates of the spots was also measured. Glycine, alanine, aspartic acid, and isoleucine were found in the liquid phase; also, Oró refers to the production of valine and leucine in other experiments in which C_2- and C_3-hydrocarbons were used. He also obtained the amides, asparagine, and glycinamide, which probably played a part in the synthesis of polypeptides (see below); this is an entirely new result.

Using a spark discharge on a gaseous mixture of $NH_3 + CH_4 + H_2$ for 100–200 h, Grossenbacher[40] analysed the products on an automatic amino-acid analyser and found the following amino-acids: 2 moles of aspartic acid, 4 of threonine, 14 of serine, 16 of glycine, 14 of alanine, 4 of lysine, 2 of leucine, 2 of isoleucine, and 1 of glutamic acid; he also found some peptides (see below).

Dose and Rajewsky[41] subjected a gaseous mixture of $CH_4 + NH_3 + H_2 + CO_2 + N_2 + H_2O$ to the action of ionising radiation (X-rays in dose of 3.5×10^6 roentgen) and found that acid and neutral amino-acids were formed. Later, Dose and Ettre[42] found that lysine and asparagine were formed, but they irradiated more complex compounds (cadaverine and alanine bicarbonates).

When a solution of ammonium acetate was irradiated with β-rays from a linear accelerator (2 MeV), glycine

and aspartic acid[43] were obtained; glycine and alanine[44] were formed by the γ-irradiation (^{60}Co, 5×10^8 r) of solid ammonium carbonate.

Palm and Calvin[19] found glycine, alanine, and aspartic acid in a mixture of $CH_3 + NH_3 + H_2 + H_2O$ which they irradiated with a beam of fast electrons (5 MeV with a dose of 10^{10} ergs).

Bakhadur[45,46] irradiated a mixture of paraformaldehyde, potassium nitrate, iron(II) chloride, and water under a 500–1000 W electric lamp and reported a large number of amino-acids in the product; however, his papers do not give sufficient grounds for his assumptions about the composition of the products and the mechanism of their formation. This remark also applies to the author's suggestion that it is possible to synthesise amino-acids by illuminating a mixture of paraformaldehyde, colloidal molybdenum oxide, and water, nitrogen being obtained by atmospheric fixation.

Finally, the formation of amino-acids by *heating* initial solutions has been studied in detail by Oró and coworkers[47,48]. In the first paper it was shown that a number of amino-acids (glycine, alanine, serine, aspartic acid, and threonine) can be obtained simply by heating aqueous mixtures of formaldehyde and hydroxylamine to 80–100° for 40 to 60 h, but the reaction had an appreciable velocity even at the lower temperature. The reaction mechanism here is also close to that of Strecker's syntheses, since formaldoxime and HCN are among the first reaction products of formaldehyde and hydroxylamine; the stationary concentration of these intermediates was $\sim 6 \times 10^{-3}$ M in the reaction $HCHO + NH_2 \rightarrow CH_2NOH \rightarrow HCN$; the amino-acid (mainly glycine) concentration reached 17.7×10^{-3} M. In the work described in the second paper[48], an aqueous solution of $HCN + NH_4OH$ was heated for 25 days at 75° and glycine, alanine, and aspartic acid were found amongst the products. These results have been confirmed by Lowe *et al.*[49], who heated a 1.5 M aqueous solution of NH_3 and HCN at 90° for 18 h; these workers also showed that considerable amounts of amino-acids are present in the form of peptides and other amino-acid derivatives, which are separated after the reaction products have been hydrolysed. Analysis in an automatic analyser showed the presence of leucine, isoleucine, serine, threonine, and glutamic acid (mostly serine) in addition to glycine, alanine, and aspartic acid. If the products had been hydrolysed in the work already mentioned here, a greater range of amino-acids might have been found.

Fox and coworkers[50] also heated the starting materials to obtain amino-acids but in their experiments the temperature was higher (140–200°) and the starting materials were too complex (salts of malonic acid); in our opinion this limits the value of their work.

4. POLYPEPTIDES

Lower peptides could be formed at the same time as amino-acids, but high-molecular peptides were probably formed in the later stages of evolution.

By the action of ultraviolet light on an aqueous solution of NH_4Cl in which FeS_2 was suspended, and through which methane was passed, Ellenbogen[51] observed the formation of a peptide which on hydrolysis gave phenylalanine, methionine, and valine. Bakhadur[52] and coworkers irradiated a solution of leucine and glutamic acid in the presence of sucrose with a 1000 W lamp and found that leucyl-leucine, leucyl-glutamic acid, and some other dipeptides were formed. However, both these reports lack confirmation.

Polyglycine has been obtained[53] by the action of a spark discharge on crystalline glycine at 13°, and on a 10% aqueous solution of glycine at 0°. Oró[39] has found that in addition to the production of amino-acids in a discharge, two compounds were obtained, the colour reactions and chromatographic behaviour of which indicate that they are low-molecular peptides formed with the participation of amides (see below), but the compounds were not identified. Grossenbacher[40], who made the most detailed examination of peptides formed in a spark discharge, found that the peptides he separated consisted of glycine and alanine (5 : 1), and also of glycine and isoleucine.

It is doubtful if peptides were actually formed in the work reported and, if they were formed, the amounts must have been insignificant. No doubt this is because peptides are readily degraded in a spark discharge or when they are irradiated. It is therefore natural that the formation of peptides and polypeptides should have been mainly observed when heat or catalysts were used. Fox and coworkers[54] studied the conditions for the thermal condensation of mixtures of various amino-acids. Linear polypeptides with a molecular weight up to 8600 were obtained by heating various amino-acid mixtures in the absence of water to 140–200° for several hours; the following mixtures were used: glutamic acid and glycine[55], aspartic and glutamic acids[56] (also in the presence of phosphoric acid[57]), lysine and alanine[54], glutamic acid and phenylalanine[54], and also a mixture containing an excess of aspartic and glutamic acids with 16 other amino-acids[58]. This work has been summarised by Fox[54]. It was shown by colour tests, infrared absorption spectra, solubility, electrophoretic mobility, and enzymic hydrolysis that the polypeptides obtained (Fox terms them "proteinoids") were not distinguishable from, for example, proteins of the caesin type. The preparation of poly-α-amino-acids has also been reported[60-62], but it has not been made clear how the results obtained are related to geochemical conditions.

The polypeptides prepared by Akabori[63] are of great interest; he suggested that the aminoacetonitrile formed from formaldehyde, ammonia, and HCN undergoes polycondensation on clay:

$$CH_2O + NH_3 + HCN \rightarrow H_2N{-}CH_2{-}CN + H_2O.$$

Experiments were done on kaolinite for 5 h at 130°. Side-chains could be introduced into the polyglycine obtained by reaction with aldehydes or unsaturated hydrocarbons; the molecular weight of the polyglycine was about 15 000. Unfortunately, these experiments were not further developed.

Oró[64] obtained polyglycine by heating glycinamide to 100° and also by heating glycine in 2 *N* NH_4OH solutions[65]; copolymers of eight different amino-acids were also obtained by heating the acids mixed with glycine in concentrated ammonia. The infrared and X-ray spectra of the products were examined, and they gave a positive biuret reaction. As has been pointed out already[49], considerable amounts of peptides have been obtained by heating an aqueous solution of HCN and NH_4OH.

5. PURINE AND PYRIMIDINE BASES. NUCLEOSIDES AND NUCLEOTIDES

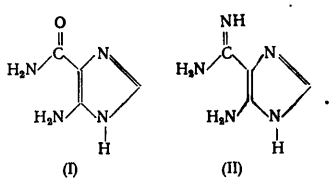
Apart from proteins, nucleic acids are the most important compounds of biological significance; for this reason,

a number of attempts have been made to synthesise nitrogenous bases, and also nucleosides and nucleotides. The main work in this field is due to Oró and Ponnamperuma.

On the action of ultraviolet light there is only a short report[66] on the formation of adenine by irradiation of an aqueous 10^{-4} M solution of HCN.

A more detailed study has been made[67] of the action of a beam of electrons (4.5 MeV, 7×10^8 rad) on a $CH_4 + NH_3 + H_2O$ mixture. In this irradiation the intermediate is HCN; according to Oró's scheme (see below) condensation of HCN leads to the formation of adenine. This purine base may be obtained because it is the most stable to radiation.

The majority of purine and pyrimidine bases were, however, obtained by Oró and coworkers[68-71] by heating aqueous solutions of HCN of various concentrations in aqueous ammonia to 70–90° for several days; in some experiments temperatures lower than 70° were also used. Adenine was obtained in this way[68] and its presence was demonstrated by eight different methods; Fig. 2 compares the ultraviolet and visible spectra of the picrates of the compounds separated with the spectra of a standard preparation of adenine. Fig. 3 shows Oró's mechanism for the formation of adenine, which is the product of condensation of five HCN molecules. It was shown that 4-aminoimidazole-5-carboxamide (I) and 4-aminoimidazole-5-carboxamidine (II)[69] were formed as intermediates; the compounds were separated and identified by various methods:



(I) (II)

Guanine was obtained from (I) by condensing it with guanidine in aqueous solution in closed vessels at 100–130°, and condensation with urea gave xanthine. Hypoxanthine (Fig. 4) was obtained from (I) by condensing it with formamidine and subsequently eliminating NH_3. The formation of adenine and hypoxanthine was also demonstrated when HCN + NH_4OH were heated at 90° for 18 h.[49]

Oró[70,71] also obtained pyrimidine bases (uracil and cytosine) by condensing other nitriles (aminopropionitrile or acrylonitrile) with urea at 135° in aqueous ammoniacal solutions. Uracil was also obtained by heating together malonic acid and urea in phosphoric acid solution at 100–140° for 1–2 h.[72]

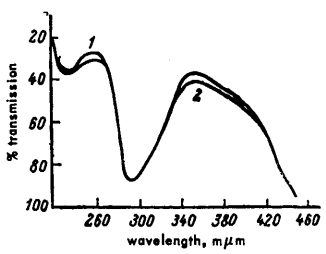


Fig. 2. Ultraviolet and visible absorption spectrum of picrate of standard adenine (1) and picrate of adenine obtained[68] from hydrogen cyanide (2).

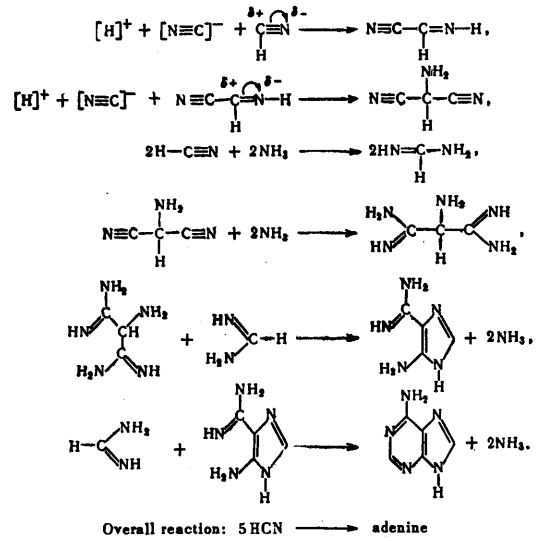


Fig. 3. Mechanism of formation of adenine from hydrogen cyanide[69].

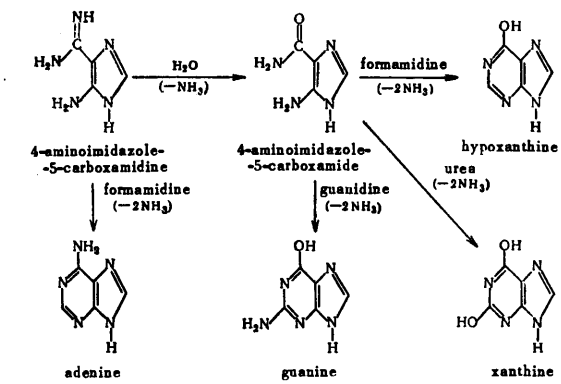


Fig. 4. Proposed mechanism for the synthesis of purines on the primary Earth[70].

The next important step was made by Ponnamperuma and coworkers[73], who showed that ultraviolet irradiation of an aqueous solution of adenine and ribose (2537 Å, 1 h, dose 10^8 r, 40°) in the presence of phosphoric acid (or better ethyl metaphosphate) caused them to condense to give the nucleoside adenosine, although the yield was very low (0.01%); the quantum yield of the process was 10^{-5}. It was also found that the nucleoside phosphates or nucleotides (adenylic acid, ADP, and even ATP) were obtained in 0.05–0.08% yield in the presence of ethyl metaphosphate; irradiation of a mixture of AMP and ethyl metaphosphate gave ATP in 0.3% yield[66,74].

Schramm and coworkers[75] have drawn attention to the catalytic part played by polyphosphates in the adenine–ribose condensation, but in Ponnamperuma's work in addition to its catalytic action the phosphate is directly included in the nucleoside, thanks to activation by ultraviolet rays. Because of the high stability of adenine to radiation, the accumulation of ATP and other adenine nucleotides takes

preference over the formation of nucleotides with other nitrogen bases. Since ATP is an energy-rich compound, which is characteristic of all forms of living organisms right down to the simplest, it is likely that organisms would have available pre-formed ATP and some other nucleotides at their origin.

6. CARBOHYDRATES

The formation of carbohydrates was in itself of great importance, since these compounds form an important biochemical class; moreover, ribose and deoxyribose were required for the formation of the nucleosides and nucleotides mentioned above.

As has been pointed out, formaldehyde was one of the main primary starting materials. Since the classical synthesis of Butlerov, it has been shown that formaldehyde could be condensed to form carbohydrates, and this subject has been repeatedly reviewed in the literature. Recently [76], it has been shown that when formaldehyde is condensed in a basic medium, up to 30 monosaccharides are formed, mainly pentoses and hexoses, which are the most stable simple carbohydrates; ribose was among the products. The intermediates included glycollic aldehyde, glyceraldehyde, and dioxyacetone [77,78]. Oró [70] obtained 2-deoxyribose and 2-deoxyxylose in ~5% yield by condensing acetaldehyde and glyceraldehyde in aqueous systems in the presence of bivalent metal (Ca^{2+}, Mg^{2+}) oxides at temperatures from 0° to 50°.

Ponnamperuma [79] has reported the formation of ribose and deoxyribose among other products when a 3×10^{-4} M aqueous solution of formaldehyde was subjected to ultraviolet irradiation.

7. ALDEHYDES AND ORGANIC ACIDS

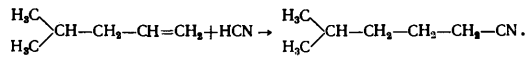
The formation of the lower aldehydes, formaldehyde and acetaldehyde, was of great practical importance for the production of amino-acids and carbohydrates and their oxidation led to the formation of a number of organic acids; as mentioned above, the preparation of amides of organic acids was an important intermediate step in the formation of nucleic acid fragments.

When ultraviolet rays act on gases of a reductive atmosphere, lower aldehydes and organic acids are among the primary compounds formed. Thus the action of rays of wavelength 1850 and 2537 Å on a mixture of $C_2H_6 + NH_3 + H_2O$ gave formic, acetic, and propionic acids [24]; with rays of wavelength 1295 Å acting on a mixture of $CO + H_2$ or CH_4, formaldehyde and glyoxal were obtained [11]; formaldehyde was obtained by the action of rays of wavelength 1450 Å on a mixture of CO, CH_4, or C_2H_6 with water vapour. The following mechanism has been proposed [10] for the formation of formaldehyde in hydrocarbon–water mixtures:

$$2H_2O \rightarrow 2H + 2OH \rightarrow H_2O + H_2 + O,$$
$$CH_4 \rightarrow CH_3 + H,$$
$$CH_3 + O_2 \rightarrow CH_2O + OH.$$

Losanitsch [80] observed the formation of aldehydes when electrical discharges acted on $CO_2 + CH_4$. Various organic acids were obtained in Miller's experiments [13,34], including formic, acetic, propionic, lactic, and glycollic; formic acid was the most abundant (23 mmoles). We found that formic, acetic, and traces of propionic acid are formed by the action of discharges on a mixture of $C_4H_{10} + H_2O$. [28] Frank found only formic acid in the acid fraction of a mixture of isooctane and water that had been subjected to discharges [38]; he explains this by the fact that only CH_3 radicals are eliminated in the degradation of linear hydrocarbons (*cf.* p. 517).

Frank obtained organic acids in higher yield by the action of discharges on the mixtures $CH_4 + H_2 + NH_3$, $CH_3OH + NH_3$, and isooctane + NH_3, all in the presence of water vapour. Since the intermediate compound in these mixtures is HCN, its addition to the terminal double bond of an unsaturated hydrocarbon probably leads to the formation of a nitrile, oxidation of which gives fatty acids (in Frank's work these were obtained in the non-volatile fatty acid fraction):



The formation of formaldehyde, formic acid, and some other acids was also observed [18,43,44] when various ionising radiations acted on aqueous solutions of CO_2 and NH_4 and Na bicarbonates.

Oró found [47] that formic acid, acetic acid, glycollic acid, and lactic acid were formed by heating a 0.25 M solution of CH_2O and $NH_2OH.HCl$ to 100°; the acids were separated and identified by column chromatography. Lowe and coworkers [49] also mention the formation of fatty acids.

8. AMINES AND AMIDES

In addition to amino-acids and organic acids, the formation of amines and amides has been mentioned in a number of papers. Formamide has been obtained [81] by the action of short-wave ultraviolet radiation (1850 Å) on a mixture of $NH_3 + CO$, and urea has been obtained by the action of rays of wavelength 1800–1450 Å on a mixture of the same composition (also with the addition of $CH_4 + H_2O$). [9] Hydrazine and hexamethylenetetramine have been obtained [10] by the action of rays of wavelength 1450 Å on a mixture of CH_4 (or C_2H_6) + $NH_3 + H_2O$; hexamethylenetetramine was also formed by 1850 Å radiation acting on a mixture of $CH_2O + NH_3 + H_2O$. [31] When a mixture of formaldehyde and ammonium salts was irradiated [28] a fraction containing methylamine, ethanolamine, isopropylamine, urea, and hexamethylenetetramine was separated.

Miller [13] obtained urea and *N*-methylurea (total amount 2×10^{-5} moles) by the action of electrical discharges on a mixture of $CH_4 + NH_3 + H_2 + H_2O$; methylamine and ethylamine were obtained by the action of a corona discharge on the same mixture [82]. Thiourea and thioacetamide have been obtained [14] by the action of a discharge on a mixture of $CH_4 + NH_3 + H_2S + H_2O$, and urea has been obtained [83] from a mixture of $N_2 + H_2 + CO$.

Oró obtained aliphatic amines, asparagine, and glycinamide by the action of a spark discharge (7 h, 15–30 kV) on a mixture of $CH_4 + C_2H_6 + H_2O$ over conc. NH_4OH. The two amides are significant not only because they are the direct precursors of amino-acids, but also because of their participation in the formation of polypeptides (see above). By heating conc. HCN and NH_4OH to 70° Oró and Kimball obtained [69] glycinamide, formamide, and formamidine. According to these workers [4], the hydroxylamine used in

their reactions might have been formed by the recombination of NH_2 and OH radicals contained in materials from comets.

A considerable amount of urea was obtained[19] by the action of a beam of electrons (5 MeV) on a mixture of $CH_4 + NH_3 + H_2 + H_2O$. Heyns and coworkers[84] noted the formation of a number of guanidine compounds when a discharge was passed through a mixture of $CH_4 + NH_3 + H_2O$, but they added a certain amount of oxygen to the mixture on the assumption that this is formed in the photodissociation of water. There are no other references to the formation of guanidine compounds.

9. IMIDAZOLE COMPOUNDS

Imidazole compounds form an important group, being intermediates in the formation of nucleic bases (see above), which are also closely connected with the formation of histidine and histamine. 4-Aminoimidazole-5-carboxamide and the corresponding amidine have been formed[69] by heating a mixture of HCN + NH_4OH. The formation of imidazole, 4-hydroxymethylimidazole, and 4-methylimidazole has been shown to occur[28] in a mixture of $CH_2O + NH_4NO_3$ exposed to ultraviolet light (2537 Å); when a mixture of $CH_3CHO + NH_4NO_3$ was irradiated, in addition to the foregoing compounds 2-methylimidazole, 4,5-dimethylimidazole, and an unidentified compound, probably an alkylimidazole, were also obtained; however, the presence of histidine could not be demonstrated in the irradiated solutions.

10. PORPHYRINS

The formation of tetrapyrrole compounds was of great importance for the subsequent development of catalase activity[7] and for the formation of the main compound that absorbs visible light in the process of photosynthesis. Chichibabin[85] obtained pyrrole by heating acetylene and NH_3 in the presence of sesquioxides. Szutka and coworkers found that tetraphenylporphyrin was formed by the action of γ-rays (^{60}Co, 5×10^5 r h^{-1}, 10 h)[86] or ultraviolet rays (3000 Å, 5×10^{16} quanta-seconds on irradiated surface)[87,88] on a mixture of pyrrole and benzaldehyde in the presence of zinc acetate. Rothemund[89] synthesised porphyrin by heating a mixture of pyrrole and formaldehyde in methanol and pyridine in sealed ampoules. Krasnovskii and Umrikhina[90] obtained porphyrin by heating (8–10 h, 100°) pyrrole and formaldehyde in methanol containing 10% of water; the reaction was accelerated by water, oxygen, and some catalysts.

11. GENERAL REMARKS

It is now known with sufficient certainty that a large number of diverse compounds of biochemical importance could have been formed by the action of various kinds of energy (ultraviolet, electrical discharge, ionising, and thermal) on the simplest compounds (CH_4, NH_3, HCN, CH_2O, etc.) that could exist under primary Earth conditions, although these simple compounds were themselves rather antibiogenic. Of necessity, this review has been restricted to those compounds of biochemical importance (amino-acids, purines, pyrimidines, organic acids, etc.), which can be obtained experimentally direct from primary non-biological substances, since the number of secondary biochemically important compounds which can be obtained in this way is very great and could only be touched on here.

In all the reactions for the formation of biochemically important compounds from simple primary substances, a prerequisite for a yield of the products was their rapid removal from the reaction zone, to avoid destruction of the compounds formed. Favourable conditions were created at the points of contact of two different reaction zones, for example, at a water surface absorbing the products of ultraviolet radiation from the atmosphere, and also at zones due to a cold atmosphere, electrical discharges, or volcanic eruptions. In all cases the accumulation of products in the ocean was of great importance[1]; at sufficient depth the absorbed compounds were protected from ultraviolet and ionising radiations and so preserved from further degradation. The quantity of organic compounds that could have settled from the primary atmosphere in 1000 million years is ~ 1 kg cm^{-2}; according to Urey[2] and Sagan[7] this would give a concentration of $\sim 1\%$ at the end of the time interval.

The work covered in this review shows that extraordinarily diverse biochemically important compounds could have been formed in the early stages of the Earth's development, but many problems have, of course, been left unsolved. Only half the amino-acid components of proteins have been obtained experimentally. Either suitable abiogenic methods of synthesis have not been found for the other amino-acids, or they were formed as secondary products, or even by biosynthesis in living cells. It is possible that the primary polypeptides or protein-like compounds did not contain a full complement of amino-acids, but they may nevertheless have had catalytically active groupings. For example, the active centres of the present-day enzymes, phosphoglucomutase, trypsin, and chymotrypsin contain the amino-acid sequence aspartic acid–serine–alanine (Asp–Ser–Ala), a sequence that might have occurred in primary polypeptides. However, many amino-acids such as histidine and cysteine that have not been obtained experimentally from primary materials play an important part in the active centres of enzymes. Elucidation of the possibility of their abiogenic synthesis would be of great interest.

In general, the problem of preparing polypeptides of fairly high molecular weight on suitable catalysts without the use of organic solvents, high temperatures, or complex organic amino-acid derivatives has received little attention; an interesting attempt at such a polymerisation[63] under the geochemical conditions of the primary Earth was not sufficiently developed.

Closely linked to the polycondensation of amino-acids on catalysts is the important problem of the origin of the optical activity of natural amino-acids. Up to now the absolute asymmetric synthesis of L-amino-acids by means of circularly polarised light has not been achieved; in all the work dealt with in this review the amino-acids were obtained as racemates, and all known methods of making optically active compounds are based on the use of existing optically disymmetry (compounds, crystals, adsorbents, etc.)[91]. Stereospecific polymers with spatially arranged side groups can be prepared on catalysts having no optical activity; in our opinion[92], the elucidation of this is of the greatest importance. It is possible that optical asymmetry developed not by the initial formation of optically active monomers and their conversion into optically active polymers, but by the reverse process; high-molecular-weight asymmetric cata-

lysts might have been formed by stereospecific polymerisation and then the secondary optical symmetry of low-molecular compounds might have developed on the basis of the polymers. The appearance of optically asymmetric and catalytically active polypeptides was important for accelerating the reaction and was therefore secured by evolution. The conditions for the formation of such polypeptides are still unknown and their experimental preparation would be a significant achievement.

A great achievement of recent years, apart from the preparation of amino-acids, has been the abiogenic synthesis of purine and pyrimidine bases, some nucleosides and mononucleotides, and also ATP (Oró; Ponnamperuma and coworkers). The preparation of such complex compounds is, of course, of great interest not only in connection with the conditions for the formation of such important compounds as nucleic acids, but also because it raises the whole question of the length of the biological stage in the Earth's evolution. Since such important compounds as nucleotides and ATP, which were previously considered to be products of the biological stage of evolution, have now been obtained by abiogenic synthesis under relatively simple conditions, the chemical stage of evolution can be reduced to 1000–1500 million years, and the origin of life can be extended into the depths of time; according to Sagan's estimate[7], life might have originated 4000 million years ago. This would explain the discovery of fossil algae in rocks 2700 million years old, or the appearance of signs of an oxidative atmosphere on the Earth 3400 million years ago[7].

It is well known that ATP passes through all the evolution of living things from the simplest organism to man; if ATP were entirely a product of biological evolution, uncountable generations would have been required for the formation of ATP precursors. Recent experiments have shown that this assumption is unnecessary and that primary living organisms could have obtained ATP in a prepared form from the surrounding medium[73]. The abiological formation of ATP was considered by Blum[93], but experimental confirmation of this possibility was only obtained recently. If ATP was present its participation in the synthesis of polypeptides or polynucleotides may be assumed. The important problem of the conversion of nucleotides into polynucleotides, similar to the simplest nucleic acids, has still not been solved experimentally under the geochemical conditions of the primary Earth. It is possible that in the presence of nucleoside diphosphates and triphosphates further condensation could occur by the Kornberg–Ochoa mechanism, the low specificity of the catalysts present and the slowness of the process being compensated for by geological periods of time.

The formation of simple carbohydrates, including such important compounds as glucose, ribose, and deoxyribose has been demonstrated experimentally beyond doubt[70,79]. In contrast, the important problem of the formation of higher fatty acids has not been solved experimentally; these formed the main basis for lipoprotein membranes and films. The interaction of higher hydrocarbons with HCN in a discharge may have been important here (p. 520), or the fatty acids may have originated at a stage when the Earth's oxidative atmosphere had been formed. The formation of porphyrins undoubtedly occurred in the later stages of chemical evolution, or even at the initial stage in the evolution of primary living organisms[3].

The mechanism and kinetics of none of the syntheses mentioned here have been studied; up to now attention has been directed to the qualitative composition and the yields of the unusually diverse products of these syntheses.

Available results show that polypeptides and polynucleotides could have arisen independently of each other under the conditions of the primary Earth. Polynucleotides could have been formed by mutual union; these would, of course, be very different from existing specific nucleoproteins but they would have the important property of forming coacervate layers due to the mutual saturation of polar groups and reduction in solubility. Although coacervates may be formed by low-molecular compounds (*e.g.* phenol–water) of limited solubility, typical coacervates are formed from compounds of high-molecular-weight, in particular from proteins and polysaccharides, two proteins with very different isoelectric points, mixtures of proteins and nucleic acids, etc. Oparin and coworkers[94] have obtained coacervates from polypeptides and polynucleotides. Thus at the state of formation of polynucleotides, or even earlier, the formation of complex molecules inevitably gave rise to more or less complex systems.

Within such systems of molecules (coacervate drops, etc.) new molecular interactions occurred that do not occur in dilute homogeneous solutions. In particular, the inclusion of catalysts in these systems led to differences in concentration between the drop and the medium and automatically converted them into chemically open macrosystems constantly exchanging matter with the surroundings.

Open systems, the stability of which was dynamically maintained by chemical reactions in the medium must have been of great evolutionary importance. These processes have been experimentally examined in simple equilibrium coacervates[95] and also in stabilised suspensions of enzymes, the stability of which resulted from the dynamic balance of surface precipitation forces of the stabilised surface layer and its enzymic hydrolysis from inside the drop[96]. In more ideal types of enzyme coacervates, the stabilising membrane was a product of synthetic reactions in the drops, and their stability resulted from the dynamic balance of chemical synthetic and degradation reactions in the drops; this made the behaviour of these systems similar to that of the simplest living organisms.

At the limit of the origin of primary living organisms, macromolecules were hardly characterised by a rigid definite specificity in their composition, but probably differed significantly from existing types of these molecules; for example, protein-like compounds might not have had a full complement of amino-acids, and nucleic compounds might have contained only relatively simple nucleotides. Division of the coacervate drops occurred with a very low specificity for transmitting "genetic information", and the development of nucleic acid and nucleoprotein molecules that ensured a higher level of specificity for this transmission might have been the result of long evolution[97]. The idea that life originated at the moment when there was a synthesis[98] coded by nucleic acids, of specific protein-like compounds is, in our opinion, erroneous; this interpretation disregards a tremendous initial period in the evolution of living organisms. It is difficult to imagine how the existing mechanism for the biosynthesis of proteins with matrix, information, and soluble nucleic acids, necessarily involving ATP and a number of amino-acids, could be built up to any extent before the origin of life, as Buchanan[99] suggests. All these multi-stage controlling processes could only have been built up in morphologically specialised open chemical systems exchanging matter with their surroundings. At a definite stage in the development of such

systems, the system as a whole and not just one component (either protein or nucleic acid) might have been reproduced. It is probably at this stage that the first living beings arose†.

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† *Note added in proof*. After this review had been written, some papers appeared that we were unable to include in the text; they are however included in the list of references. These additional references are: a review[100], an asymmetric Strecker synthesis of L-alanine based on *d*-methylbenzylamine[101], an examination of the conditions for the formation of the Earth's primary atmosphere[102], a paper on the chemical evolution of the primary Earth[103], and also a paper on the thermal synthesis of natural amino-acids under primary atmosphere conditions[104].

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POLYMERIC BORON COMPOUNDS

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In the three years since the publication of our earlier review of the scientific literature on polymeric compounds containing boron[1], the number of papers published in this field has considerably increased, as well as their penetration of the subject. Investigators no longer restrict themselves to reporting the production of a polymer, but now describe its properties, give the results of investigations which confirm its structure, and, in particular cases, draw conclusions regarding the features of behaviour which reflect the specific chemical nature of boron.

However, as a whole, the chemistry of polymeric boron compounds still lags far behind the monomeric chemistry of boron in time spent on it and in the vigour of its development. It is as though it were passing through an induction period of hidden development, which is necessary for the assimilation of the huge amount of original material made available by the monomer chemistry and for the working out of the basic methods for the production of the polymers.

In this review we follow the order of presentation of material used in our previous review.

Only a few polymers are known in which the main chain contains B–B bonds. Thus Kuchen and Brinkmann[2] reacted metallic sodium with phenylboron dichloride and obtained the linear polymer of composition $[(C_6H_5)B]_n$ having molecular weight 820, corresponding to $n = 9–10$. The product is a yellow amorphous powder which is slowly oxidised in air and darkens above 200°, and it was considered to be the phenyl derivative of the previously described linear polyboron hydride $[BH]_x$.[3] A polymer of analogous structure was obtained by the pyrolysis of tricyclohexylboron, with elimination of cyclohexene and cyclohexane[4]:

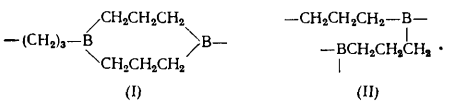
$$x\,B(C_6H_{11})_3 \xrightarrow{250^\circ} (BC_6H_{11})_x + x\,C_6H_{10} + x\,C_6H_{12}.$$

In their investigation of the chemical reactions of diboron tetrachloride, Holliday and coworkers obtained a solid polymeric boron subchloride $[BCl]_n$ from it by pyrolysis[5], and reacted it with epoxyethane to obtain tetrakis-(2-chloroethoxy)diboron $B_2(OCH_2CH_2Cl)_4$ which decomposes on heating to give the polymer $(BOCH_2CH_2Cl)_n$.[6]

According to a British patent[7], tetraethoxydiboron $B_2(OCH_2CH_3)_4$ is also converted into a polymer on heating at 100°.

The pyrolysis of decaborane gives hydrogen and a condensation product $B_{20}H_{24}$, which can evolve further hydrogen and is converted into a non-volatile solid boron hydride[8].

New polymers containing B–C bonds in the main chain have been described. These are most simply prepared by hydroboration of unsaturated compounds; thus by the action of diborane on triallylboron Mikhailov and Pozdnev[9] obtained a solid polymer which they consider contains both cyclic (I) and acyclic (II) units:



(I) (II)

According to patent data a polymer of structure (I) can be obtained by the hydroboration of allene [10].

A solid polymer insoluble in ether has been prepared from 1,2-diphenyldiborane and cyclopentadiene [11]. The polymers, in which all three valencies of the boron are bonded to carbon, are very readily oxidised in the air; they have no independent application, therefore, and are known only as intermediate products in the conversion of dienes into the corresponding glycols, generally $\alpha\omega$-glycols, or into the polymethylene diboronic acids $(HO)_2B(CH_2)_nB(OH)_2$. [12]

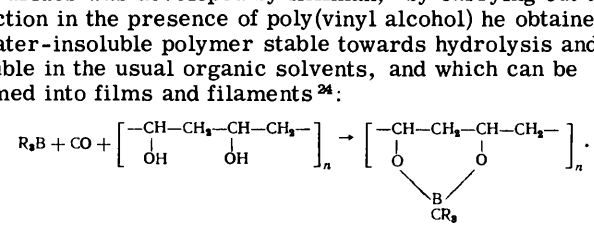
Solid polymers stable to heating and containing boron and carbon in the main chain can be obtained by reacting lower esters of orthoboric acid or boron halogenides with phenylene-1,4-di(magnesium bromide) [13] or by pyrolysing diphenylboron chloride in the presence of aluminium chloride [14]. These polymers have the structure $(-C_6H_4BOH-)_n$.

The production and properties of polymers with a carbon main chain and with boron in side-chains have been more fully investigated. Such compounds can be prepared by polymerising vinyl derivatives of borane or boric acid and its esters or anhydrides. Methylvinylborane and ethylvinylborane can polymerise spontaneously during their preparation [15]. *p*-Vinylbenzeneboronic acid polymerises on heating or in the presence of free-radical initiators. The polymer is a polyelectrolyte, soluble in aqueous alkali and in many organic solvents containing 5–10% of water, stable on heating to 300°, but losing water above this temperature to give boric anhydride [16]. The cyclic tris-(*o*-vinylphenyl)boroxin can also polymerise [17].

The polymerisation of the dibutyl ester of vinylboronic acid under the action of atmospheric oxygen or heat has been studied by Mikhailov and Aronovich, who concluded that molecular oxygen forms a copolymer with the partially hydrolysed vinylboronic ester. The dibutyl ester was also copolymerised with ethyl vinyl ether and with styrene [18].

Vinylbenzeneboronic ester polymers and copolymers with vinyl acetate, acrylonitrile, styrene, and vinyl chloride have been recommended for moulding, the preparation of laminar plastics, and as coatings, impregnants, and adhesives [19-21]. Polymers of vinylboronic, divinylborinic and propenylboronic acid and their copolymers with isocyanates can be used as boron-containing plastics [22]. Polymers are known in which boron in a side-chain is attached to the main carbon chain through oxygen. Kolesnikov and coworkers prepared the mixed anhydride of dibutylborinic and methacrylic acids: $(n\text{-}C_4H_9)_2B\text{–}OCOC(CH_3)=CH_2$ and its polymer and copolymers with methyl methacrylate and styrene. They obtained viscous liquid, waxlike, or vitreous polymers, insoluble in the usual organic solvents but soluble in dimethylformamide [23].

A new and original preparation of substituted boric acid anhydrides was developed by Hillman; by carrying out this reaction in the presence of poly(vinyl alcohol) he obtained a water-insoluble polymer stable towards hydrolysis and soluble in the usual organic solvents, and which can be formed into films and filaments [24]:



A polyester has been prepared by boiling boric acid with a hydrolysed copolymer of vinyl acetate and alkenes, of hydroxyl group content 17.3%, in xylene [25].

Carbon-chain polymers with boron in side-chains have also been described in Braun's review [26].

Methods for the preparation of B–N polymers are being vigorously developed. New methods for the production of boron nitride have been described: by reaction between boric acid and urea [27] and between diborane and hydrazine in the flame of a special burner [28].

In the reaction between hydrazinium sulphate and lithium tetrahydroborate, Goubeau and Ricker [29] obtained first the borine–hydrazine complex $BH_3.H_2NNH_2$; on heating this was converted into the hydrazobisborane $H_2B.HN.NH.BH_2$, and further pyrolysis produced the unstable compound $(HBN)_n$, still containing N–N bonds, and which is liable to explode.

The action of hydrazine on tris(dimethylamino)boron gives a readily hydrolysed polymer of composition $B_2(HNNH)_3$. [30]

From the reaction between diboron tetrachloride and hydrazine, Holliday obtained the new boron nitride $(B_2N_2)_n$, in which the B–B and N–N bonds are still retained. This nitride is less stable thermally than the two previously known nitrides [6].

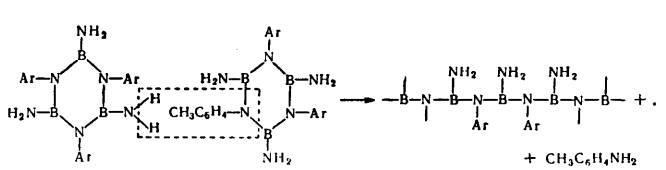
Linear B–N polymers are still very few, although much effort has been devoted to their preparation. The conditions for preventing ring formation in the reaction between primary amines and organoboron dichlorides have been most fully investigated by Gerrard. Using butylamine or isobutylamine and phenylboron dichloride, he showed that the alkyl group of the amine sterically hinders ring formation, so that the only reaction product is a linear polymer with B–N bonds; this is a solid substance, readily hydrolysed in boiling water [31,32].

In analogous investigations with 1,2-diphenyldiborane and amines or organoboron diamines, Korshak *et al.* [33] were only able to prepare linear polymers with very short chains, for example, using cyclohexylamine, the dimer:

$$(C_6H_{11})\,NHB\,(C_6H_5)\,N\,(C_6H_{11})\,B\,(C_6H_5)\,NH\,(C_6H_{11}).$$

An attempt to increase the length of the molecule by polycondensation of this dimer by heating to 260° only led to its decomposition. The comparatively large radical on the nitrogen apparently produces steric hindrance to chain lengthening as well as to ring formation [33].

It has not been shown possible to produce linear B–N polymers by opening the ring of borazoles with polymerisation of the resulting biradical, although two patents recommend carrying out this reaction in the presence of alkaline catalysts [34,35]. Recently Gerrard *et al.* [36] pyrolysed *BB'B''*-triamino-*NN'N''*-tri-*p*-tolylborazole and found that the borazole ring opened with the formation of a branched polymer with linear units as a result of transamination:

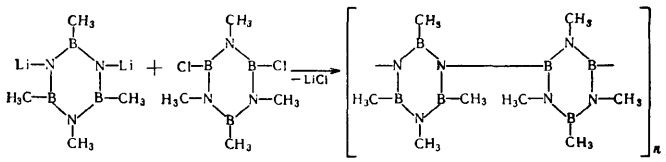


The polymer dissolves in some organic solvents and is not hydrolysed by atmospheric moisture.

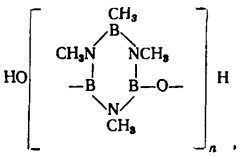
Considerably more is known of polymers in which the main chain consists of borazole rings joined either directly

by covalent bonds, or by amino-nitrogen, a polymethylene, or arylene chain, or hetero-organic or inorganic chains.

By condensing *NN'*-dilithiotetramethylborazole with *BB'*-dichlorotetramethylborazole Wagner and Bradford[37] obtained a polymer of molecular weight 1382 and softening point 155°:

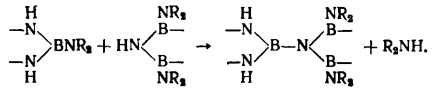


By quantitative hydrolysis of *BB'*-dichlorotetramethylborazole they also obtained the polymer of structure:



of molecular weight 3512 and m.p. 180–200°; the presence of a B–O–B bond was proved by infrared spectroscopy[37].

In their study of the pyrolysis of *B*-(dialkylamino)borazoles, Gerrard and coworkers[38] observed the formation of a B–N bond between different rings:

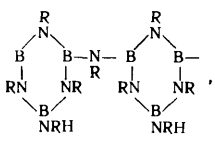


The ability of borazoles having unsubstituted nitrogen to undergo polycondensation was also observed by Meller, who obtained non-volatile vitreous products by heating *BB'*-di-n-butyl-*B"*-chloroborazole and *BB'B"*-tris(triphenylsiloxy)borazole[39].

The action of ionising radiation on *BB'B"*-trimethylborazole has given a polymer of $M = 1100$, soluble in organic solvents, and in which the main chain contains borazole rings; it was thought that the borazole radicals produced by the radiation react with further borazole molecules to form the polymer, with elimination of H_2 and CH_4.

The formation of individual linear units by elimination of rings is also possible[40].

The previously known polymer consisting of borazole rings joined by amino-nitrogen:



was described by Lappert[41].

A detailed investigation of the transamination of *B*-aminoborazole has been made by Niedenzu and Dawson, who obtained *BB'B"*-trihydrazinoborazole, which when heated is converted into a highly cross-linked polymer[42,43].

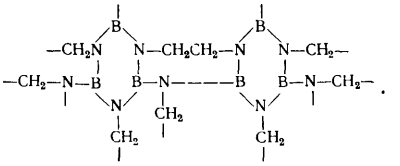
Polyborazoles in which borazole rings are joined by a hydrocarbon chain have often been described. The most important of these are the products of the polymerisation of *BB'B"*-triallyl-*NN'N"*-triphenylborazole and *NN'N"*-triphenyl-*BB'B"*-trivinylborazole and the copolymerisation of these with vinyl monomers. Because of the trifunctionality of the borazole monomers, the main hydrocarbon chains include borazole rings also.

Pellon and coworkers[44] have conducted a systematic investigation of the polymerisation of such monomers and the effect of steric factors; they obtained gel-like polymers of comparatively low molecular weight.

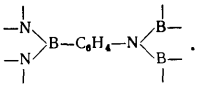
The production of solid polymers and copolymers of *BB'B"*-triallyl-*NN'N"*-triarylborazoles and *BB'B"*-trivinyl-*NN'N"*-trialkylborazoles has been described in American patents[45,46].

Ruigh has studied the polymerisation of *BB'B"*-tris-(2-chlorovinyl)borazole; by carrying out the reaction in boiling acetone, he obtained a solid vitreous polymer, probably of linear structure[47].

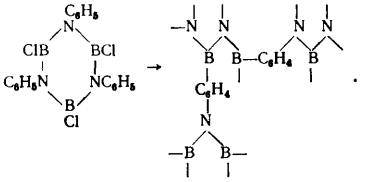
By reacting thioborates with ethylenediamine, Shchegoleva *et al.*[48] obtained a polymer which apparently has the structure:



Methods of joining borazole rings using bifunctional compounds have been developed by Gerrard and coworkers. By heating *BB'B"*-trichloro-*NN'N"*-triphenylborazole at 300°, HCl was given off and a polymer was produced which infrared spectroscopy showed to contain B–C bonds, so that the polymer was assigned the structure[31]:

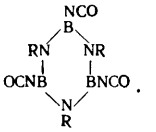


However, Gerrard later refined his results, and came to the conclusion that the borazole ring opens during the pyrolysis, the reaction more accurately proceeding[36]:



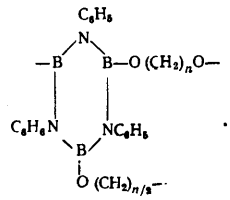
An attempt to obtain polyborazoles by pyrolysis of complexes of boron halides with diamines, in particular the 2 : 1 complex formed between boron trichloride and *p*-phenylenediamine, gave an infusible and insoluble polymer of composition $[ClBNC_6H_4NBCl]_n$. Whether the polymer was linear or polycyclic could not be diagnosed from the complex infrared spectra observed[49].

Lappert and Pyszora prepared a number of boron isocyanates and isothiocyanates, including a borazole with isocyanate-groups on the boron atoms[50]:



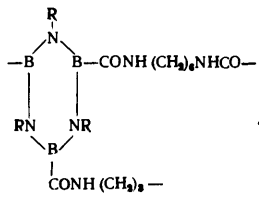
With hexamethylenediamine or phenylenediamine this gave three-dimensional polymers which were insoluble in organic solvents and boiling water[51].

Polycondensation between *NN'N"*-triphenylborazole and diols or polyols, with elimination of hydrogen, enabled Korshak *et al.* to obtain a number of rubberlike polymers, both of linear structure and of the branched structure:

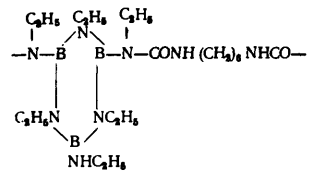


These polymers are very unstable towards hydrolysis, and decompose when kept in contact with air[52].

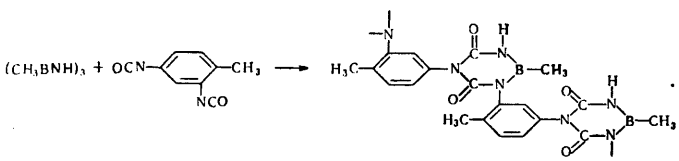
The migration copolymerisation of *NN'N"*-trimethylborazole and *NN'N"*-triphenylborazole with hexamethylene diisocyanate produces high-melting polymers, of low sensitivity to atmospheric moisture, of the structure[53]:



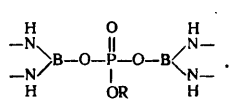
BB'B"-triethylamino-*NN'N"*-triethylborazole has also been copolymerised with hexamethylene diisocyanate, producing a linear polymer, melting at 185–200°, of the structure[54]:



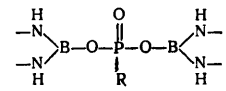
The borazole ring of *BB'B"*-trimethylborazole is decomposed on reaction with 4-methyl-1,3-phenylene diisocyanate with the formation of a polymer[55]:



High-melting thermostable polymers, sensitive to atmospheric moisture, have been obtained in which borazole rings are joined by phosphoryl or phosphonyl radicals; thus Gerrard and coworkers[56] condensed chloroborazoles with phosphoric esters to produce a polymer containing the unit:

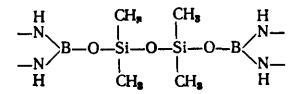


Phosphonic esters have given polymers with the unit[57]:

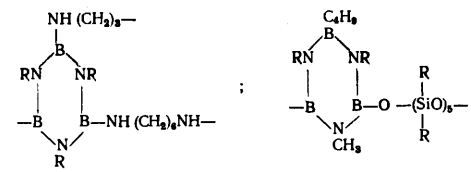


(R = H, C_2H_5, CCl_3, or Cl).

Korshak *et al.*[58] obtained a similar polymer from *BB'B"*-trichloroborazole and dibutyl methylphosphonate. By condensing *BB'B"*-trichloroborazole with tetramethyldisiloxanyl dibutyl ether, they produced a polymer melting above 300° and with a reduced viscosity in cresol of 0.16. It is unaffected by atmospheric moisture. The borazole rings in this polymer are joined by siloxane bridges[58]:



Polycondensation of *BB'B"*-tri-n-butylthio-*NN'N"*-trialkylborazoles and *B*-n-butyl-*B'B"*-di-n-butylthio-*NN'N"*--trialkylborazoles with hexamethylenediamine and various diols, including siloxanediols, led Mikhailov and Galkin[59] to obtain a number of interesting three-dimensional and linear polymers:

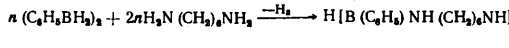


Those obtained from hexamethylenediamine were infusible and thermostable, but could be hydrolysed; those containing siloxane bridges are not hydrolysed in the air.

Various polymers of different structure and properties in which the main chain consists of B, N, and C atoms have been described, generally linear but sometimes cross--linked.

In their investigation of the donor properties of nitrogen in the ethylenediamine–diborane complex, Holliday and Jeffers[60] found the latter to give off hydrogen and to be converted into a polymer. Krause refers to similar polymers in his review of boron compounds[61].

Korshak *et al.* showed[62] that 1,2-diphenyldiborance gives linear polymers on reaction with hexamethylenediamine, *p*-phenylenediamine, or *NN'*-diisopropylhexamethylenediamine:

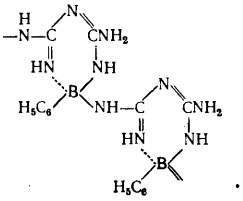


The presence of N–H bonds was shown by infrared spectroscopy and by reaction with isocyanates.

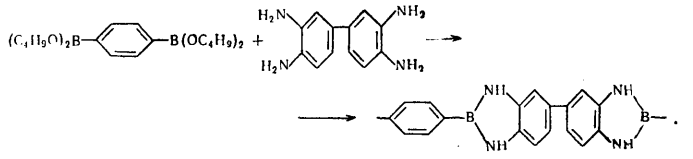
Free benzeneboronic acid can also react with diamines; with ethylenediamine it forms a brown water-soluble vitreous polymer melting at 80°.[63]

Organoboron diamines are also able to react by transamination with diamines, giving resinous products whose structure and properties have been little studied[64,65].

The transamination reaction between phenylbis(dimethylamino)boron and biguanide has been described; the infusible and insoluble polymer obtained has the structure[66]:



A very thermostable polymer has been obtained by condensing dibutyl benzene-1,4-diboronate with an aromatic tetramine as shown:



The polymer loses 25% of its weight when heated to 800° in nitrogen[67].

A solid high-molecular product, very sensitive to atmospheric moisture, has been prepared by the polymerisation of dimethylboron isocyanate $(CH_3)_2BNCO$.[68]

Linear polyboroureas have been obtained by copolymerising organoboron diamines with hexamethylene diisocyanate:

$$R'NH-\underset{R}{B}-NHR' + OCNR''NCO \longrightarrow -N-\underset{R'}{B}-\underset{R'}{N}-CONHR''NHCO-.$$

The solid vitreous products have melting points ranging from 50° to 200°, depending on the substituents on the boron and nitrogen. They are unaffected by moist air, but most are hydrolysed in boiling water[69].

The production of three-dimensional polymers of analogous structure from tri(alkylamino)borons and diisocyanates has been proposed in patents; suggested uses include the formation of films and shaped objects[70,71].

Ruigh and coworkers[72] copolymerised benzeneboronic acid with diisocyanates. Hexamethylene diisocyanate gave a hard film of poly(hexamethyleneurea), from which all the boron could be extracted by methanol in 70 hours without destroying the film.

According to other patents, free boric acid can also produce polymers with isocyanates[73]:

$$2\,H_3BO_3 + 3OCNRNCO \longrightarrow [B_2(NRN)_3H_4]_n + CO_2.$$

Most information on B–P polymers is still contained in patents. A few papers have described methods for the production of linear polymers. The pyrolysis of borane–secondary phosphine complexes first gives the linear polymer $-PR_2-BH_2-$, which on heating above 200° is almost completely depolymerised, with formation of cyclic trimers. According to Burg, this reaction is caused by the P → B donor bond from unit to unit along the whole length of the open chain of the molecule, so that at one end there should be a $R_2PH \rightarrow B$ bond, and at the other a free pair of electrons on phosphorus. At elevated temperature the donor bond may be displaced three units along the chain, and the terminal R_2P of the grouping can close the ring of the trimer[74]. With depolymerisation by such a mechanism, blocking the terminal groups with tertiary amines or phosphines suffices to render the linear polymer stable to heating above 250°.[75]

Linear and cyclic phosphinoborines have been prepared from trimethylsilylphosphine and diborane or dialkylboron halides:

$$(CH_3)_3SiPR_2 + R'_2BCl \longrightarrow (R_2PBR'_2)_n + (CH_3)_3SiCl.$$

The Si–P bond is easily broken, and many alkyl- and aryl-phosphinoborines can be obtained in high yield[76].

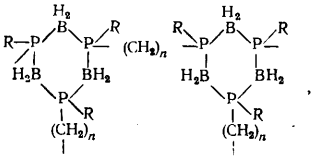
Attempts to prepare phosphinoborines by reacting the dimethylaminophosphines $P[N(CH_3)_2]_3$, $CH_3P[N(CH_3)_2]_2$, and $(CH_3)_2PN(CH_3)_2$ with BR_3, BF_3, or BCl_3 have been less successful; in most cases the corresponding complexes were not produced, but exchange took place, for instance CH_3PCl_2 and $(CH_3)_2PCl$ were obtained in the reaction with BCl_3.[77]

Burg and Brendel[78] have suggested a method for producing linear bis(trifluoromethyl)phosphinoborine $[(CF_3)_2PBH_2]_n$, which is thermally and chemically stable.

Primary phosphines have a greater tendency to form linear B–P polymers, because of the presence of hydrogen atoms on the phosphorus; Burg and Wagner have proposed methods for the production of such polymers[79], which on heating lose hydrogen and take on a cross-linked, reticular structure[80].

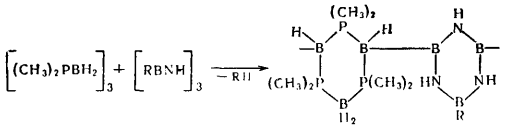
Pyrolysis of the phenyldichloroborine–phenylphosphine complex gives a polymer $[-P(C_6H_5)B(C_6H_5)-]_n$ which is thought to be linear[81]; according to patent data, this polymer melts at 142–144° and is readily soluble in alcohol[82].

Patents describe the preparation of polycyclic phosphinoborines of the type



in which the rings are joined by polymethylene or phenylene bridges; they are obtained from secondary biphosphines $HRP(CH_2)_nPRH$ and diborane or from difunctional boranes $X_2B(CH_2)_nBX_2$ and phosphines R_3P.[83]

Trimeric dimethylphosphinoborine has been condensed with *B*-substituted borazoles:



(R = C_4H_9 or C_6H_5) to give solid infusible polymers insoluble in the usual solvents[84].

It has recently been found that higher boron hydrides can be used to obtain B–P polymers of increased chemical and thermal stability. Thus Burg has prepared the polymer $\{B_2H_5(CH_3)_2P[N(CH_3)_2]_{0.4}\}_x$ by reacting pentaborane B_5H_9 with $(CH_3)_2NP(CH_3)_2$. This polymer becomes thermoplastic above 200° and is an excellent dielectric[85].

Condensation polymerisation of bis(chlorodiphenylphosphine)decaborane with bis(hydroxydiphenylphosphine)decaborane has produced a polymer of molecular weight 27 000:

$$n\,ClP(C_6H_5)_2B_{10}H_{12}P(C_6H_5)_2Cl + n\,HOP(C_6H_5)_2B_{10}H_{12}P(C_6H_5)_2OH + 2n\,(C_2H_5)_3N \longrightarrow$$
$$\longrightarrow [-OP(C_6H_5)_2B_{10}H_{12}P(C_6H_5)_2-]_{2n} + 2n\,(C_2H_5)_3N.HCl.$$

Heating to 320° does not affect the inorganic main chain, but even at 270° hydrogen is given off (probably from the decaborane residues).

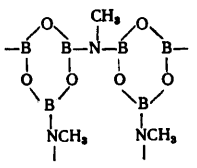
Reaction of bis(azidodiphenylphosphine)decaborane with 1,2-bis(diphenylphosphino)-ethane or -benzene also gives polymers[86]: (R = C_2H_4 or C_6H_4)

$$N_3P(C_6H_5)_2B_{10}H_{12}P(C_6H_5)_2N_3 + P(C_6H_5)_2RP(C_6H_5)_2 \longrightarrow$$
$$\longrightarrow 2_nN_2 + [=P(C_6H_5)_2-R-P(C_6H_5)_2=N-P(C_6H_5)_2B_{10}H_{12}P(C_6H_5)_2-N=]_n.$$

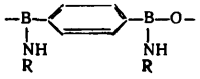
The production of phosphine–borane complexes and cyclic phosphinoborine trimers, including those substituted on both phosphorus and boron, has been described in several patents[87–91].

Boron- and halogen-containing cyclic phosphinoborines have been obtained by heating dialkylphosphinoborines with excess of alkyl halide in the presence of aluminium halides. The products are high-melting and, like the non-halogenated phosphinoborines, chemically inert[92]. The borohalogenation of polymeric phosphinoborines has been claimed[93].

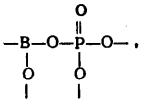
Polymers containing B–O (anhydride) bonds have been described; thus polycondensation of *BB'B''*-tri(methylamino)boroxole has given a polyboroxole, stable to heat but susceptible to hydrolysis, in which the individual rings are joined by an imino-group[94]:



Tetrabutyl benzene-1,4-diboronate condenses with amines and diamines to give high-melting air-stable polyaminopolyanhydrides[95]:

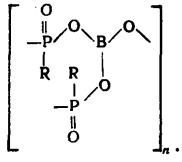


A boric and phosphoric mixed anhydride polymer, stable to hydrolysis and having the reticular boron phosphate structure:



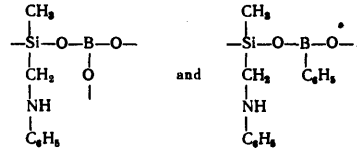
has been prepared by Gerrard and coworkers[96] by pyrolysing the complex $(RO)_3P{=}O.BCl_3$ at up to 1000°.

Phosphonic esters react with boron trichloride to produce analogous polymers which are high-melting and hydrolysed by aqueous alkali[56]:



Boric acid and its alkyl esters have been very successfully used for modifying siloxane rubbers, the anhydride bonds B–O–Si being formed[97–99]; in particular, the introduction of $-O-\underset{|}{B}-OC_4H_9$ groups improves the stability towards thermal oxidation, the elasticity, and other properties of polysiloxanes[100].

Borosiloxane elastomers can be protected against ease of hydrolysis by irradiation[101] or by the introduction of polar groups into the polymer chain; for instance, polymers containing phenylaminomethyl groups bonded to silicon are more stable to hydrolysis than poly(boro-organosiloxanes) not containing amino-groups[102,103]:



Organic boron–silicon polymers suitable as components of thermostable adhesives have been obtained by the polycondensation of boric acid with phenyltriethoxysilane and methylphenyldiethoxysilane[104].

A method has been proposed for the preparation of the vinyl-, methylvinyl-, and divinyl-polysiloxane borates of composition (for the vinyl compound) $[CH_2{=}CHSiO_3B]_n$, which are polymeric powders insoluble in the usual solvents and hydrolysed by water[105].

Polyesters of boric acid with polyols and hydroxyamines and mixed polyesters of boric and certain dicarboxylic acids have been described. The polyesters of boric acid with polyols are thermostable substances, but are not high-melting and are sensitive to hydrolysis by atmospheric moisture; they are completely hydrolysed in boiling water. The polyesters of boric acid with hydroxyamines are stable to hydrolysis, and many are soluble in water[106].

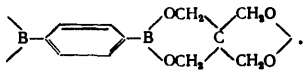
Oligomeric polyborates of aldoses, ketoses, and pentoses containing 8–10% of boron and stable when heated to 200–230° have been prepared[107].

Polyesters of boric acid with glycol or hydrogenated castor oil have been recommended as lubricants[108], and a polyester of boric acid with glycerol has been suggested as a vitreous binder[109].

Polymers from esters of polyepoxy-acids and boric acid, which are not hydrolysed by hot water, have been proposed as foam plastics and as protective and flame-resistant coatings[110].

trans-Cycloalkanediols give non-volatile polymeric esters with butaneboronic acid, but the *cis*-diols have only produced the monomeric cyclic esters[111].

Polyesters of aliphatic and aromatic diboronic acids are known, and are more stable to hydrolysis because of the intramolecular rings which they contain; thus moist air does not affect the polyester produced from benzene-1,4-diboronic acid and pentaerythritol, of the structure[112]:



Polyesters of diboronic acids with tetrakis-(2-hydroxyethyl)polymethylenediamines are completely stable to

hydrolysis and are fairly thermostable, and can be used for the production of films and fibres [113-115].

Polymers containing B–S bonds have been reported comparatively recently. These vitreous polymers of composition $(RSBH_2)_n$ (where R = CH_3, C_2H_5, and n-C_4H_9) were prepared by reacting diborane with the appropriate mercaptan. The methylthioborane polymer is stable on storage, but the ethyl and butyl compounds became converted into the corresponding trimers [116]. The polymers react with olefinic hydrocarbons to produce dialkaneborinic esters [117], *e.g.*:

$$[C_4H_9SBH_2]_x + 2xCH_2 = CH_2 \longrightarrow x\,(C_2H_5)_2\,BSC_4H_9.$$

Up to the present no commercially acceptable boron-containing polymeric materials have been described which possess the whole range of desired properties, *i.e.* more stable to heat than purely organic compounds, satisfactorily stable chemically and to hydrolysis under conditions of use, and suitable for fabricating or for direct use. Most of the known polymeric boron compounds are solid, thermostable (but infusible), insoluble materials which are not workable, and they are also insufficiently stable towards hydrolysis. However, there are no grounds for doubting that polymers could be obtained which satisfy all these basic demands. This is indicated by the ability of boron atoms to form stable covalent bonds with O, N, P, C, and H atoms and with other boron atoms, the ease of formation of coordination bonds, as a consequence of the high electron unsaturation, and the tendency to form numerous cyclic structures, which is due to the valency characteristics of boron. These are favourable indications that thermostable polymers could be produced. The ease of hydrolysis may be suppressed by making use of donor–acceptor bonds, cyclisation, and steric factors.

Organoboron polymers will probably find wide application. Polymers with a high boron content, for example those based on higher boron hydrides, may be of use as protective media against irradiation by slow neutrons. The thermoplastic linear polymers consisting of linked boroxole, borazole, or phosphinoborine rings can be used for the production of fibres, films, coatings, and adhesives, and, because of their high adhesion to glass, as compositions in heat-resistant glass–plastic materials. Polymers which can form reticular structures may be used as thermally reactive binders, for example in Triplex. Trimeric cyclic and polymeric phosphinoborines are of value as high-quality dielectrics.

There is much significant material on boron-containing polymers in previously published reviews and monographs [6,36,61,75,118-120].

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COMPOUNDS WITH CONJUGATED DOUBLE BONDS

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I. INTRODUCTION

The term "compound with conjugated double bonds" applies to a wide variety of organic substances, both monomeric and polymeric, and showing large differences in physical and chemical properties. We shall use it to describe a compound containing a fairly large number of carbon–carbon double bonds alternating with single bonds. The double bonds may include hetero-atoms, *i.e.* atoms with free electron pairs (such as N, O, S), without perturbing the conjugated system. These substances are intensely coloured, have a relatively high electrical conductivity, and show anomalous magnetic properties (electron paramagnetic resonance signals and static paramagnetism). We may arbitrarily classify these compounds into two general groups: 1) polymers with conjugated bonds and hetero--atoms in the conjugated chain, and 2) organic dyes. The second group includes polynuclear aromatic hydrocarbons, although these do not give an electron paramagnetic resonance signal.

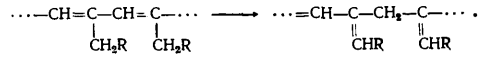
The special magnetic and electrical properties of polymers and other compounds with conjugated double bonds have received attention from many investigators in recent years[1–5]. In this review an attempt is made to expand systematically the results of the various investigators in this field, but monomeric or polymeric chelate compounds[6], polymers with a chain of metal atoms, or recently synthesised (and of independent interest) polymers with conjugated triple bonds[7] will not be considered here.

II. METHODS OF PREPARATION

The preparation of dyes has been reviewed recently[8,9]. Polymers with conjugated double bonds are prepared by a variety of methods, the most important of which are listed below.

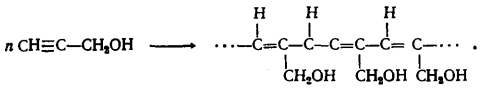
Polymerisation of acetylene hydrocarbons. Acetylene can be polymerised to give a system of conjugated bonds by various catalysts: aluminium ethoxide containing $TiCl_4$, titanyl or vanadyl acetylacetonates[10–12], sodium tetrahydroborate with a nickel halide[13] or an organophosphorus complex[14]. Polymerisation occurs between +80° and -80°; the number of units in the black, insoluble polymers is 12–15. Benzene is also formed in good yield.

The aliphatic homologues of acetylene undergo an analogous polymerisation[15], but they do not give conjugated systems, probably because of the isomeric rearrangement.



This type of rearrangement has also been reported in poly(cyclohexylacetylene) prepared by thermal polymerisation[16].

The polymerisation of acetylene can be induced by radiation at very low temperatures, giving a brown *cis*-polymer in the liquid phase and a dark red, insoluble *trans*--polymer in the solid phase[17]. Radiation polymerisation of propynol in the liquid or solid phase produces a dark red *trans*-polymer:



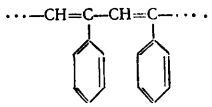
Phenylacetylene can be polymerised either by heating in an argon atmosphere or in the presence of air[18,19] for 6–12 h, or in the presence of a catalyst[19,20] at 80°. Initiators have little effect on the yield of the polymer, which does not exceed 30%. According to the polymerisation temperature used (150–400°), the resulting polymers vary in colour from yellow to black, the molecular weight also increasing with the depth of colour. The yield of polymer increases very significantly at polymerisation pressures of 98 and 588 MN m^{-2}†, reaching 66–67% at temperatures as low as 120°. The mean molecular weight of the polymer[21] can reach 1200. Alternatively, the yield of polymer can be increased by raising the polymerisation time to 18 h or by heating in solution in xylene or chlorobenzene

† 98 066.5 N m^{-2} = 1 kgf cm^{-2}, in accordance with the SI international system of units [for the SI system see Russ.J.Inorg. Chem., 8, 1481, 1484 (1963) (Ed. of Translation)].

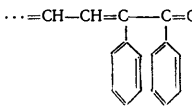
for 48–65 h. The yield of polymer is 75% in the first case, and practically quantitative in the second, but the mean molecular weight[22] does not exceed 1020.

The polymerisation of phenylacetylene can also be induced by irradiation with fast electrons or γ-rays[23,24], giving a molecular weight of up to 1700. The rate of polymerisation is independent of the dose rate, increases linearly with the integral dose of irradiation between wide limits, and is relatively insensitive to temperature.

It is assumed in all the above papers that the poly(phenylacetylene) molecules take up the "head-to-tail" (*i.e. trans-*) configuration with respect to the double bonds:



However, the "head-to-head" structure is proposed for poly(phenylacetylene) in a recent study[25] of the kinetics of its thermal polymerisation, in which various polymeric fractions of molecular weight 306–1700 were isolated.

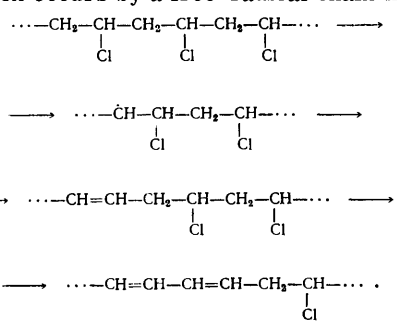


Polymerisation of the "head-to-tail" type is said to produce triphenylbenzene, and cause chain breaking.

It has recently been shown[26] that polymerisation of phenylacetylene on a Ziegler catalyst can give a product of mean molecular weight 5000, and polymerisation on copper oxide in a flow system (250–350°) can achieve a molecular weight of 7000. A mixture of aluminium ethoxide and bis-(dimethylglyoximato)iron gives an even higher degree of polymerisation when used as a polymerisation catalyst for phenylacetylene[27]: the mean molecular weight of the soluble fractions reaches 8900, and some insoluble products are formed as well. The total yield of poly(phenylacetylene) is almost quantitative.

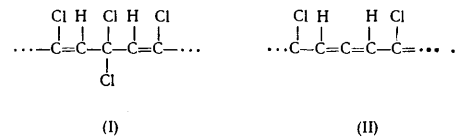
p-Diethynylbenzene polymerises easily on being heated, giving a three-dimensional polymer with conjugated bonds[28]. Furthermore, it gives copolymers with poly(phenylacetylene) and other substances. These processes are discussed in Section VII, Reactivity.

Intramolecular degradation of polymers. The most typical example of this is the formation of a conjugated chain in poly(vinyl chloride). The discoloration of poly(vinyl chloride) under the influence of light or of ionising radiation has long been recognised. However, Winkler[29] was the first to establish that a system of conjugated bonds, sometimes of quite appreciable length, is formed under these conditions as a result of loss of HCl. The degradation occurs by a free-radical chain mechanism:



The poly(vinyl chloride) molecule is branched, and at low temperatures (100–150°) the chlorine is not removed from tertiary carbon atoms: only the least stable parts of the macromolecule react under these conditions (allyl chloride and oxygen-containing groups[30]). At 190–200° the degradation occurs throughout the molecule.

Poly(vinylidene chloride) also becomes degraded with evolution of HCl, but in this case the conjugation can be perturbed (I), or allyl groups can be formed (II):



(I) (II)

The photochemical degradation of poly(vinyl chloride) also proceeds by a radical mechanism, initiated by light of wavelength[31,32] less than 310 nm. Irradiation of poly(vinyl chloride) with fast electrons or γ-rays produces chromophoric groups and polyene chains, giving rise to a colour varying from yellowish green to dark red, which gradually disappears at room temperature[33–36].

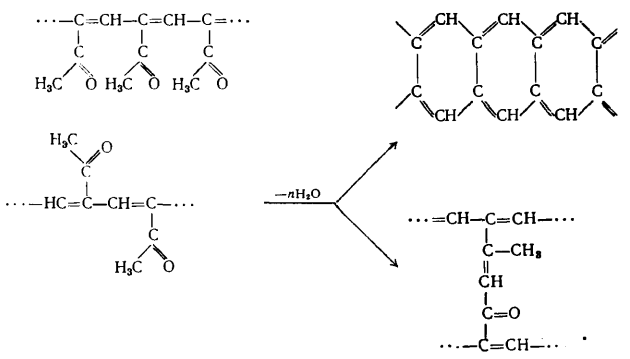
Poly(vinyl chloride) can be made to split off HCl also by chemical means. When poly(vinyl chloride) is treated with pyridine and a solution of alkali in methanol, a nitrogen-containing compound with conjugated bonds and a structure similar to that of cyanine dyes is formed[37]. A deeper (but still not complete) degradation is produced by the action of morpholine in a nitrogen stream[38] at 166°. The most effective dehydrochlorinating agents are the alkoxides, their efficiency increasing with the length of the alkyl chain (up to 99,6% dehydrochlorination has been reported[39]). The whole of the HCl is easily removed from poly(vinyl chloride) and poly(vinylidene chloride) with sodium pentyl oxide[40]. Treatment of poly(vinyl chloride) with potassium amide in liquid ammonia at room temperature gives a polyene containing 12% O, of composition[41] $CH_{1,12}O_{0.11}$. The dehydrochlorination of poly(vinyl chloride) by alkali treatment requires the presence of zinc chloride and a temperature[42] of 250°.

A linear or three-dimensional polyene is easily formed by heating poly(vinyl bromide). This material can be shaped and heat-treated to give filamentary or massive specimens of polyene[43].

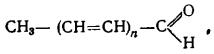
Poly(vinyl acetate) can also give a polyene with evolution of acetic acid, but this type of thermal degradation occurs only at 300° *in vacuo*[44]. A conjugated structure can be obtained much more easily by treating poly(vinyl acetate) with *p*-toluenesulphonic acid in benzene or toluene solution; as in the case of poly(vinyl chloride), loss of acetic acid occurs also at positions removed from the double bond, but the conjugated sections are of different length and are frequently interrupted[45].

After prolonged (20–30 d) standing, followed by treatment with glacial acetic acid to remove the HCl, 2-chlorovinyl methyl ketone forms a black, insoluble polymer[46] of suggested structure $H-[C(COCH_3)=CH]_n-Cl$. In the presence of iron(III) chloride the removal of HCl is much faster. The reaction is best carried out in sealed ampoules, because appreciable quantities of the trimer are formed in an open vessel or in solution. Heating the polymer to 300–700° under 1600 N m^{-2} pressure increases the carbon content in the polymer; it is thought[47] that further polymeric condensation of the product occurs under these

conditions, both intramolecularly, to give six-membered rings, and intermolecularly:



The formation of an insoluble, coloured polymer has been observed during the polymerisation of vinyl acetate in the presence of boron trifluoride[48] or alumina–silica gel with an acidic surface[49]. In both papers, the polymer is assumed to contain a system of conjugated double bonds. It seems likely that hydrolysis of the vinyl acetate occurs first, followed by polymerisation and dehydration to give a polyene chain. The possibility of the second stage was demonstrated[50] by preparing a dark substance showing all the properties of a conjugated system, of probable structure

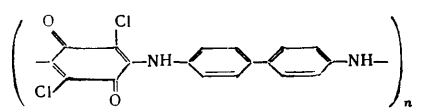


from acetaldehyde adsorbed on silica gel. The formation of polyene chains from vinyl acetate and acetaldehyde in the presence of silica gel occurs at room temperature.

When polyethylene is irradiated with neutrons or fast electrons, *trans*-vinylene bonds are formed, but not in large numbers: one double bond per 200 carbon atoms[51] after 4.65 MJ kg^{-1}. At the same time, cross-linking of the polyethylene molecules occurs. Irradiation in the air produces even fewer double bonds and less cross-linking in the polymer.

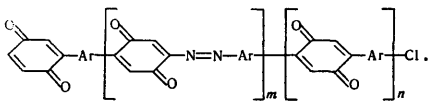
Polyethylene has also been irradiated in a reactor (11.2–250 MJ kg^{-1}) with subsequent heating in air[52] to 250–900°. The irradiation appears to give rise to six-membered saturated rings; the formation of conjugated double bonds is brought about by the subsequent oxidation of the polymer. The products of irradiation and heat treatment are black, infusible powders.

Polymeric condensation of diamines with carbonyl compounds. The reaction of chloranil with benzidine in alcohol, in the presence of sodium acetate, produces black infusible materials[53,54] to which the following structure has been ascribed:

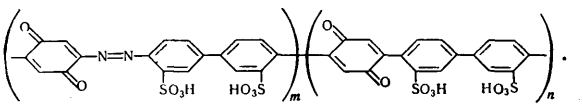


In a medium of dimethylformamide the chlorine atoms can be replaced by acetate groups. Similar polymers have been prepared by the reaction between *p*-benzoquinone and *p*-phenylenediamine, or benzidine and 3,3-benzidinedicarboxylic acid[55]. The terminal groups are amino-groups with chloranil and quinone groups with benzoquinone, the number of monomer units is 5–10.

Polymeric compounds are obtained also if the appropriate bisdiazo-compounds are used instead of the diamines[56]. The structure of these polymers is the following (where Ar denotes an aromatic residue):

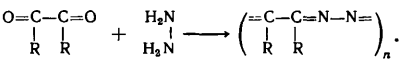


The number of polymeric links is 5–15. Azo-groups are retained in the polymer because of incomplete decomposition of the diazo-compounds. They cannot be completely removed, but polymers containing as little as 0.5% of nitrogen have been prepared. Polymers have been prepared, by the same method, from the diazo-compound of 4,4′-diaminobiphenyl-3,3′-disulphonic acid, taken in threefold and fourfold excess over benzoquinone[57]:



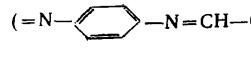
The nitrogen content of this polymer is 0.55–0.75%.

Polymeric condensation can occur also through carbonyl groups. Thus, the reaction between hydrazine and diacetyl or other diketones, and also with glyoxal, yield polyazines[58,59]:



The carbonyl groups can be separated by intervening atoms or groups. Polyazines containing oxygen and sulphur atoms in the chain, and also CH_2, OCH_2, and C_6H_4 groups, have been synthesised in this way. The glyoxal derivative is black, the other polymers vary from light green to orange in colour. The number of units in the polymer is 23–25 with benzil, and probably higher still with glyoxal, but it falls to 4–7 when intermediate groups are introduced into the chain.

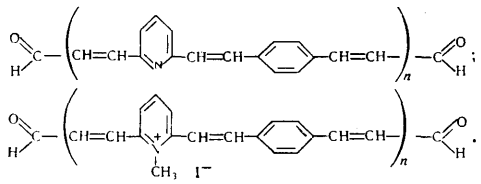
The polymeric condensation of glyoxal, terephthalic aldehyde, and diacetyl with *p*-phenylenediamine at 80° leads to the formation of polymeric Schiff bases[60]. In the last two cases the chemical composition of the polymer agrees with that calculated for a dimeric product. The number of monomer units in the polymer



has not been determined.

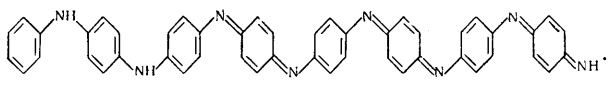
Aromatic dialdehydes, when condensed with 2,6-lutidine at 160–220° or with *N*-methyllutidinium iodide at 70–90°.

give brown infusible polymers which probably have a linear structure[61]:



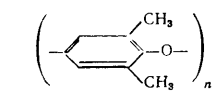
The number of polymeric units is 9–11 in the former material, 4–7 in the latter.

Oxidation of aromatic amines and phenols. The product of the oxidation of aniline by potassium dichromate (aniline black) has been known for a long time, but its structure is not fully characterised despite the large number of investigations devoted to it[62–64]. We only know with certainty that aniline black belongs to the class of polymers with conjugated double bonds. The product of the oxidation of aniline by potassium chlorate, nigraniline, also belongs to this class[62,64], as is clear from its formula:



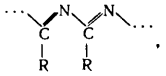
The oxidation of aniline, diphenylamine, and triphenylamine by sulphuric acid leads to the formation of dark-coloured products reminiscent of aniline black, but containing sulphur[65].

Linear polyphenylene oxides may be formed during the oxidation of sterically hindered phenols, owing to the stability of the phenoxy-radicals. Thus, when air is passed through a solution of 2,6-dimethylphenol in pyridine in the presence of copper(I) chloride, a linear polymer of the following structure is formed[66,67]:



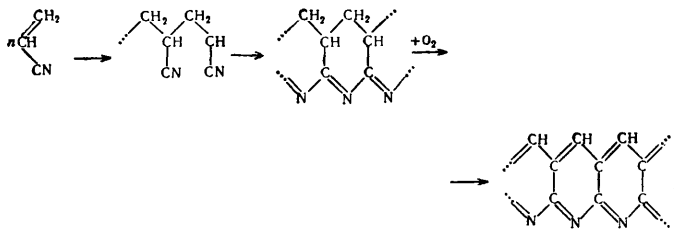
Oxidation proceeds with the participation of Cu^+ ions, since the same polymer can be obtained also in the absence of oxygen. Products of similar structure are formed from 4-chloro- and 4-bromo-2,6-dimethylphenol[68], and also from 2,6-diethylphenol, 2,6-diphenylphenol, and other compounds of this class[69].

Polymerisation of compounds containing the CN group. When hydrocyanic acid is refluxed with aqueous ammonia or potassium cyanate, a dark brown, insoluble polymer is formed. This compound, an acylaminic acid, has a cyclic structure and contains amino-groups[70]. Aliphatic and aromatic nitriles can form, in the presence of metal chlorides, linear polyconjugated systems of the type



whose properties depend on the polymerisation time[71].

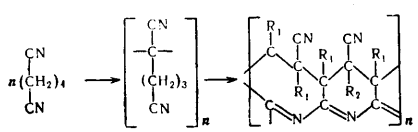
Polymerisation of acrylonitrile, followed by heat treatment at 400–500°, yields coloured polymers[42,72,73]. The relevant processes here are the formation of condensed six-membered rings and their dehydrogenation:



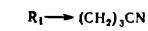
Previous irradiation at -196° lowers the temperature at which conjugated chains appear in polyacrylonitrile to 135–175°.[17]

Heat-treatment of poly(methacrylonitrile) also produces the conjugated chain –C=N–C=N–, but aromatisation of the rings does not take place because there are no CH groups[74]. The formation of conjugated bonds is accelerated by nucleophilic reagents such as acids, which can form copolymers with the substance or remain within the polymer. Cyclisation of poly(methacrylonitrile) can also be induced by irradiation in the liquid or solid phase[17].

The formation of cyclic structures is not confined to hydrogen cyanide and poly(acrylonitrile). Polymerisation of tetracyanoethylene at 200° in the presence of catalysts[75] also leads to a black product for which a structure similar to that of porphyrin has been proposed. Cyclic polymers can be obtained also from aliphate nitriles, but this requires either irradiation in the solid phase[17] or a stronger oxidising agent than atmospheric oxygen. Treatment of glutaronitrile or of the nitrile of methylmalonic acid with an excess of t-butyl peroxide produces black powdery polymers having a cyclic structure[76], which are formed by the scheme:



where



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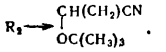
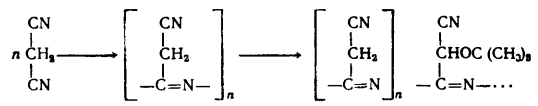


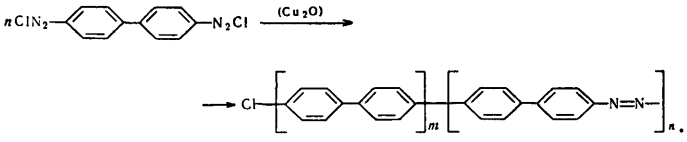
A polymer of malononitrile is formed at a 2.5 : 1 molar ratio of nitrile to peroxide, but it is not cyclic:



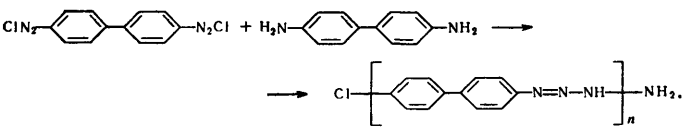
The number of monomer units in the polymer can be as high as 90–100. This process is a typical application of the polymeric recombination reaction[77].

Polymerisation of bisdiazonium compounds. This rather specialised method of preparation of

polymers with conjugated double bonds consists in the low-temperature polymerisation of the bisdiazonium compounds of aromatic diamines in the presence of copper(I) oxide[78,79]:

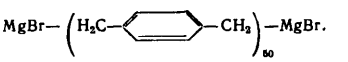


The products of this reaction are known as polyazophenylenes. Complete removal of the azo-groups from the polymers has proved impossible so far. Nonetheless, the conjugation of the polymers is not disturbed, due partly to the linearity of their structure. Later, polyazophenylenes with various substituents in the benzene rings (CH_3, COOH, etc.) were also prepared[80-82]. The bisdiazonium salt of benzidine copolymerises with benzidine, giving a linear polytriazine[83]:



Starting from the bisdiazonium compounds of 4,4'-diaminodiphenylmethane and 4,4'-diaminodibenzil, polymers with $-CH_2-$ and $-CH_2CH_2-$ groups between the benzene rings have been prepared[84]‡.

Wurtz reaction. Using this simple method, polyphenylenes[85,86] have been obtained from *p*-dichlorobenzene, and polyxylylenes and polyphenylenemethylenes[87,88] from compounds of the type $ClCH_2-Ar-CH_2Cl$ (where Ar is an aromatic hydrocarbon residue). The polymers were strongly branched in both cases. The action of magnesium on *p*-xylylene bromide gave a polymer[89] of composition

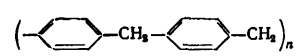


Polymerisation of aromatic compounds in the presence of metal chlorides. Benzene (1 mole) rapidly polymerises to poly-*p*-phenylene[90] in the presence of aluminium chloride (0.5 mole), copper(II) chloride (0.5 mole), and water (1 ml), at 36–37°. The reaction does not proceed in the absence of either of the chlorides. Replacement of the copper(II) chloride by iron(III) chloride seems to lead to polymers with a cellular structure, since their C : H ratio fluctuates between 1.8 and 2.5.

The same method can be used to prepare polymers with methylene groups in the chain, *e.g.* from dichlorethane and halogen-substituted benzenes, and also from biphenyl, benzene, and dibenzyl[91,92]. The catalyst is aluminium chloride.

‡ Strictly speaking, these polymers do not possess a system of conjugated bonds, and their assignment to the type being discussed here is justified only on the basis of their magnetic properties. The correctness of this point of view is examined in Section VIII, Theory. For comparison, other methods of preparation of polyphenylenes (containing $-CH_2-$ groups) are described below.

The polymeric condensation of benzyl chloride and α-chloromethylnaphthalene has been accomplished[92] in the presence of chlorides of Group IV elements: the effect of titanium chloride was examined both with the pure monomer and in solution. Silicon and thorium chlorides are the least active. This reaction gave polymers of the type



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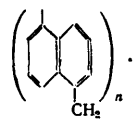
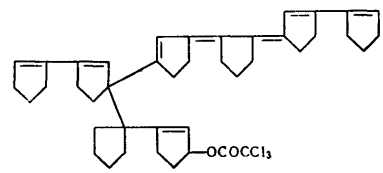
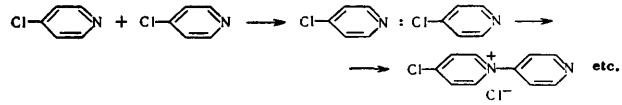


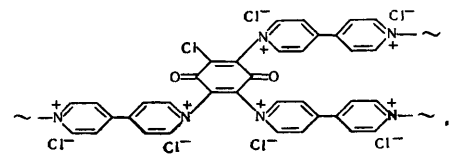
Other methods. Cyclopentadiene slowly polymerises in the presence of trichloroacetic acid, forming a system of conjugated double bonds:[94]



The polymerisation proceeds by an anionic mechanism; the number of units is not large. A polymer with conjugated bonds can also be obtained[95] by the onium polymerisation of 4-chloropyridine at 50–60°. The mechanism of this process is described by the scheme

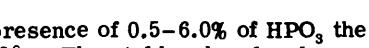


The reaction products are yellow and contain 8–14 pyridine nuclei. A copolymer of 4,4'-bipyridyl with chloroanil, having the structure



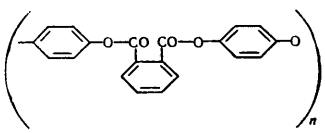
has also been prepared.

Heating the complex of pyridine with zinc chloride $ZnCl_2(C_5H_5N)_2$ to 375–400° in a dry inert medium causes fissure of the pyridine ring with formation of the linear polymer[96]:



In the presence of 0.5–6.0% of HPO_3 the reaction occurs even at 330°. The yield and molecular weight of the polymer increase to some limiting value, depending on the temperature of the experiment, at high concentrations of HPO_3.

Zinc chloride promotes various polymeric condensation processes, such as the reaction between phthalic anhydride and hydroquinone or *p*-phenylenediamine at 250°, giving polymers with heteroatoms in the conjugation chain[42]:



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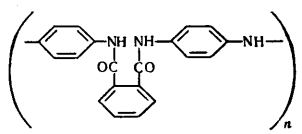


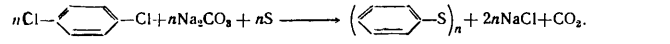
Polymeric condensation with phenols to give conjugated systems has been reported also in the case of anhydrides of other polybasic acids[97].

Aldehydes and ketones containing a methyl group are also capable of undergoing polymeric condensation in the presence of a large excess of zinc chloride or other chlorides[98]. The resulting polymers again contain conjugated bonds of the type $(CR{=}CH)_n$. The polymeric condensation of acetaldehyde proceeds at 70°, that of ketones at 180–200°.

Polyphenylenes can be prepared by prolonged (several hours) heating of organolithium compounds LiArLi, where Ar = *p*-phenylene or 4,4′-diphenylene, in ether in the presence of cobalt bromide[99]. The reaction is

$$n\,\mathrm{LiArLi} + (n-1)\,\mathrm{CoBr_2} \longrightarrow \mathrm{Li\,(Ar)_{\it n}Li} + (n-1)\,\mathrm{Co} + 2\,(n-1)\,\mathrm{LiBr}.$$

Polyphenylene sulphides[100] can be obtained by fusing *p*-dichlorobenzene with sodium carbonate and sulphur:



These polymers show strong branching. Linear polyphenylene sulphides result from the autocondensation of the sodium salt of 4-chlorothiophenol[101].

III. SOLUBILITY

Most polymers with conjugated double bonds are sparingly soluble, the solubility decreasing as the depth of colour increases. The black polymers are insoluble, as a rule. Only when nitrogen atoms are present in the conjugated chains can such polymers dissolve in concentrated acids and in some polar solvents: this has been demonstrated for poly(aminoquinone)s[56], aniline black[63], poly(azophenylene)s[80], and polytriazenes[83]. Polymeric nitriles are insoluble, however. A high proportion of the poly(phenyl sulphide) polymer is soluble in diphenyl ether[101], but up to 20% of the material does not dissolve.

Poly(phenylacetylene) and polycyclopentadiene are fairly readily soluble in benzene and other organic solvents, possibly because of the small number of monomer units in the polymeric chains[18-20,94]. The low-molecular-weight fractions of poly(azophenylene)s and polytriazenes (M = 600–700) are also soluble in benzene and acetone, and can be extracted from the main bulk of the polymer[80,83]. The specific viscosity of solutions of high-molecular fractions of these polymers goes through a maximum when plotted against concentration: this confirms that macromolecules of the polymers have a linear structure and show association. Substituents in the benzene rings of the polymers weaken the association of the macromolecules in solution.

IV. MAGNETIC PROPERTIES

Polymers with conjugated double bonds. The most characteristic feature of these polymers, which distinguishes them from other high-molecular-weight compounds, is the presence of a single, narrow electron-paramagnetic resonance (EPR) signal with a g-factor of 2.003, *i.e.* corresponding to a free electron. There have been no reports of any hyperfine structure in the EPR spectra of these polymers. The concentration of unpaired electrons per gramme of the material differs very considerably in the different polymers: from 2.4×10^{17} for phenylacetylene[18] to 8.7×10^{19} for some poly(azophenylene)s[81]. The width of the line between the points of maximum slope is 0.6–1.4 mT§ [millitesla (Ed. of Translation)]; a narrower signal is found in heat-treated poly(azophenylene)s[81] (0.3–0.6 mT), and in irradiated polyethylene[52] heated to 500–700° and evacuated to 266.6 μN m^{-2}¶ (50 μT). In both cases the narrowness of the signal is associated with the thermal treatment of the polymer. When the polymer is dissolved, neither the shape nor the magnitude of the signal are changed[19,102]†.

Poly(azophenylene)s which have not been heat-treated give a second signal of width 2.6–3.5 mT, superimposed on the first, and also a triplet signal with a g-factor of 2.05; both these signals disappear when the material is heated[81] to 300°. A fairly broad EPR signal 2.5–2.5 mT is obtained with heat-treated polyacrylonitrile[42,73] and irradiated poly(vinyl chloride)[33]. The half-width of the line for the latter material has been given[103,104] as 5.3 mT. The EPR spectrum of the oxidation products of aromatic amines by sulphuric acid contains a line of width[65] ~ 5.0 mT; for aniline black the width is[105] 1.1–1.3 mT, and for its hydrochloride[106] 0.6 mT.

In chemically dehydrochlorinated poly(vinyl chloride) the line width is[39,44] 1.1–1.2 mT. In polycyclopentadiene the signal depends on the length of the polymer chain, since it appears only 20 h after the beginning of the reaction[107]; as the number of monomer units in the polymer changes from 5 to 11, the concentration of unpaired electrons increases by one order of magnitude[108].

The EPR spectra of polyvinylenes, prepared from poly(vinyl chloride), are significantly altered by oxygen: in air the EPR spectrum is either converted into an asymmetric signal typical of peroxidic compounds[33] or disappears[41]. Organic peroxides have a similar effect[40]. Heating the material to 400° in a vacuum or in air restores the original signal. Conversely, polycyclopentadiene gives a stronger signal in air than at 1.333 N m^{-2}, but further

§ 1 T = 10^4 G, in accordance with the SI international system of units.

¶ 133.322 N m^{-2} = 1 mmHg, in accordance with the SI international system of units.

† Solutions of poly(phenylacetylene) show a poorly resolved hyperfine structure[185].

evacuation to 13.33 μN m^{-2} does not alter the signal[107]. The width of the polyethylene line decreases[52] after vacuum heat-treatment. For the remaining polymers, the intensity and width of the signal remain the same in the air and in an inert medium (nitrogen, argon).

When polymers with conjugated bonds are heated, whether in a vacuum or in air, the concentration of unpaired electrons does not normally alter. The only exception are polymers containing only carbon and hydrogen. Heating poly(phenylacetylene) (prepared at 150°) to 300° or 400° raises the concentration of unpaired electrons by one or two powers of ten respectively[19]. The EPR signal of polycyclopentadiene decreases with increasing temperature from -198° to 60°, becomes stronger at higher temperatures, and begins to drop again above 120°. The latter effect is more significant the higher the molecular weight of the polymer fraction[108]. Conversely, the concentration of unpaired electrons decreases when poly(diethynylbenzene) is heated, and at 500° *in vacuo* the signal disappears[28]. The intensity of the signal from dehydrated polyacetaldehyde decreases on heating to 200°; the effect is completely reversible[50].

In addition to narrow lines, the EPR spectrum of aniline black[105,106] and poly(aminoquinone)s[102,109] contain some broad lines (over 10 mT wide). The wide EPR signal reported for bisdiazonium copolymers with quinones[3] was not confirmed by later work[84]. These lines are similar to those found in the EPR spectra of antiferromagnetics (MnO, Cr_2O_3). The g-factor of the centre of the broad lines is different from the free electron g-factor; the calculated apparent concentration of unpaired electrons per gramme of the polymer[109] can be as high as 10^{21}.

Introduction of methylene groups into poly(azophenylene)s causes a sharp decrease in the number of unpaired electrons, but if the benzene rings are separated by two methylene groups the signal persists[84]. Poly(arylmethylene)s prepared by other methods have not been examined by EPR.

The magnetic susceptibilities of poly(phenylmethylene)s and poly(naphthylmethylene)s prepared in the presence of Group IV metal chlorides have been measured[93]. Poly(phenylmethylene)s are diamagnetic irrespective of the type of catalyst ($\chi = -0.571 \times 10^{-6}$ cm^3 g^{-1}). Poly(naphthylmethylene) prepared by block polymerisation in the presence of $TiCl_4$ is also diamagnetic ($\chi = -0.045 \times 10^{-6}$ cm^3 g^{-1}). The other polymers of this class are paramagnetic; their magnetic susceptibility depends on the type of catalyst, and reaches the value $+1.441 \times 10^{-6}$ cm^3 g^{-1} after polymerisation in the presence of $SiCl_4$.

Compacted poly(diethynylbenzene), heated at 170° in a nitrogen stream, is weakly paramagnetic; beyond 400° its susceptibility becomes negative, and beyond 500° it becomes positive once again[28]. Concentrations of unpaired electrons calculated from magnetic susceptibilities do not agree with those derived from EPR spectra.

The magnetic susceptibility of poly(phenylacetylene)[102] increases with molecular weight from 0.20×10^{-6} to $2.6 \times \times 10^{-6}$ cm^3 g^{-1}‡; poly(phenylacetylene) of low molecular weight is diamagnetic, $\chi = -0.6 \times 10^{-6}$ cm^3 g^{-1}. Blyumenfel'd *et al.* conclude[102] that the EPR signal reflects the properties of the individual macromolecule, whereas the magnetic susceptibility of the polymer is determined by its structure. The increase in magnetic susceptibility of poly(aminoquinone) after heating and addition of copper, and in that of poly(tetracyanethylene) after heating, are quoted in support of this hypothesis.

Poly(phenylacetylene) and poly(aminoquinone) show a characteristic saturation of the magnetic susceptibility with increasing field strength, similar to that of ferromagnetic materials[102]. The magnetic susceptibility of polytriazine, equal to $+0.55 \times 10^{-6}$ cm^3 g^{-1}, is independent of the field strength[83].

The nature of the anomaly in magnetic properties found in polymers with conjugated double bonds has been discussed repeatedly. Great interest was aroused by the first reports of broad EPR lines, and "ordered regions" were assumed to be present in polymers with conjugated bonds by analogy with ferromagnetic domains in which electrons can move freely[102]; the extent of these regions was thought to depend on structural factors. It was even suggested that wide lines should be regarded as a general property of polymers with conjugated bonds. The obvious absence of broad lines in the spectrum of poly(phenylacetylene) was interpreted as being due to an extremely wide line, or to measurements below the Néel point. However, the "ferromagnetic" and "antiferromagnetic" properties of polymers could be due to small amounts of paramagnetic impurities[110], to which the EPR method is very sensitive. False paramagnetism, which disappears upon the removal of impurities, has been demonstrated in other materials by EPR.[111] The broad line in the EPR spectrum of aniline black[106] is caused by the presence of Cr^{3+} ions, and disappears when these ions are removed.

The saturation level of magnetisation of various polyvinylidenes has been measured[112]. The amounts of iron oxides needed to explain the results were compared with those found experimentally. In the case of poly(phenylacetylene) the effect is undoubtedly caused by 0.01% of iron impurity; for other polymers the calculated amount of iron is higher than the experimental but in poly(diethynylbenzene) they are of the same order of magnitude. No broad EPR lines were observed. It was suggested that the regions of ferromagnetic inclusions are closely bound up with the organic structure of the polymer.

The view that wide lines are a characteristic of all polymers with conjugated bonds has again been upheld: in polyvinylenes the line becomes saturated at microwave power because of the strong spin–orbital relaxation. Results on wide EPR lines in polymers with conjugated bonds, and their interpretation, are obviously in need of clarification.

The triplet signal in poly(azophenylene)s, with a g-factor of 2.05–2.06, could also be due to impurities, although it has been ascribed[81,84] to unreacted macro-radicals. The latter do, however, account for the line of width 2.5 mT and g-factor 2.00 which is observed in irradiated poly(vinyl chloride) and poly(acrylonitrile), and also in poly(azophenylene)s.

The reason for the appearance of the narrow singlet signal is discussed in Section VIII, Theory.

Dyes and other compounds. A narrow EPR signal with a g-factor of 2.003, very similar to the signal given by polymers with conjugated bonds, has been observed in Lacmoid[113], and in cyanine[114] and triphenylmethane[115] dyes. Its intensity increases when the materials

‡ Somewhat different, but apparently less accurate, results have also been reported[19].

are cooled to -196°, and also when the pressure is reduced to 1.333 N m^{-2} and beyond. The effect of dissolution of the dye on the EPR spectrum was not established in the cases of cyanine dyes[114], but with triphenylmethane dyes it was shown that dissolution causes loss of the signal[115].

In solutions of Lacmoid the signal persists: it disappears only if the solid is heated to 730°.

Cyanine dyes give an EPR signal only if their polymethyne chain exceeds a certain length: for example, there is no signal in dyes bound by a single CH group. As the chain becomes longer, the width of the line decreases[114]. Unfortunately, the materials used in this work were not always pure, and this caused apparent exceptions to the above rule for pseudocyanines, and the alleged "discovery" of a broad signal (g = 2.240) in one of the thiacyanines.

Phthalocyanines also give an EPR signal. According to some workers[116], the signal is given only by α-phthalocyanine, obtained from the β form by reprecipitation from concentrated sulphuric acid followed by careful washing. β-Phthalocyanine, extracted by nitrobenzene and sublimed in nitrogen, does not give a signal. These reports were not confirmed, however, by later work[117], in which a weak EPR signal was occasionally (but not invariably) detected in the α modification, and a strong signal in the β modification, collected after repeated filtrations of phthalocyanine solutions in pyridine and dioxan. However, when the β-phthalocyanine was prepared by heating α-phthalocyanine *in vacuo* at 300° no signal was observed.

A broad line (g = 2.19, width ≃ 0.16 T) was noted[118] in the spectrum of metal-free phthalocyanine, and ascribed to collective interaction of unpaired electrons, although the possibility of paramagnetic impurities was admitted. The intensity of the signal increases on cooling the material, whilst dissolution in concentrated sulphuric acid suppresses the EPR signal of phthalocyanine completely.

Other workers[119] failed to detect broad lines in the EPR spectrum of "metal-free" phthalocyanine. Attempts at removing impurities by subliming the "metal-free" phthalocyanine in oxygen, nitrogen, or vacuum at 500° proved unsuccessful, since their signal persisted§. Therefore, the narrow EPR signal of phthalocyanine was ascribed[119] to the presence of impurities with an unfavourable separation factor, or to partial carbonisation.

This conclusion reappears in a number of other papers on EPR signals in dyes. Thus, no signal was found[120] in carefully purified β-carotene either in air, or in vacuum, or after heating to 130°, whereas β-carotene which has not been purified gives a strong signal[121]. The "impurity" approach to the EPR signal is most rationally developed by Kholmogorov and Glebovskii[122], who prepared a sample of phthalocyanine not giving an EPR signal by multiple reprecipitations from sulphuric acid; by contrast, the phthalocyanine precipitated from the filtrate and sublimed in a vacuum gave a signal 0.4–0.7 mT wide. Also, their original samples of triphenylmethane dyes[122] gave no signal, and only after heating them in air to 200° did a signal appear (owing to partial oxidation). The EPR signal of certain cyanine dyes is also due to oxidation products which can form even at room temperature. Thus, all the EPR spectra observed in dyes can be ascribed to the effect of impurities difficult to remove from the parent substance and which are apparently of high molecular weight, since they are formed by resinification: yet, no direct proof of the formation of such impurities during the oxidation of dyes has been given[122]. The broad EPR lines in phthalocyanines and nigrosine are unmistakably due to paramagnetic metal ion impurities.

We cannot, of course, ignore oxidation effects in dyes: this is shown by the influence of oxygen on the EPR spectrum of cyanine dyes[114], and by the appearance of an EPR signal upon oxidation of phenothiazine[123]. But there are no grounds for ascribing to them all reported EPR spectra in dyes, even though high-molecular oxidation products would go into solution with difficulty, and would always be expected to be present in the precipitate if they are present in the filtrate. To throw some light on this problem, the EPR spectra and the magnetic susceptibility of triphenylmethane dyes synthesised in a diamagnetic vessel and carefully purified have been investigated[124]. A narrow EPR signal was observed in every case, in complete agreement with previous work[115]; anisotopic diamagnetism was also detected, suggesting delocalisation of π electrons in the molecule. When the dyes are dehydrated there is a sharp drop in diamagnetic susceptibility, which can only be explained by an increase in the paramagnetism of the material resulting from the removal of the dipolar water molecules. The signal disappears in solutions, and is restored when the dye is precipitated. Thus, the paramagnetism of triphenylmethane dyes, and probably also of other dyes, is an intrinsic property of the solid phase of these materials: it arises from the same causes as the magnetism of polymers with conjugated double bonds. These are discussed in Section VIII, Theory.

Phenazhydrine in the solid state also gives a narrow EPR signal with a g-factor typical of a free electron, and which disappears in solution[125]. The intensity of the signal increases by a factor of 2–3 after heating at 120° for 30 min, but does not increase any further at this temperature.

Light-induced EPR signals in dyes have been reported in various papers. Thus, when cyanine dyes adsorbed on silver bromide are illuminated, a narrow signal (g = 2.005) is observed[126] at -196°. Heating to room temperature suppresses the signal, but on cooling and illumination the signal reappears. The cycle can be repeated several times. The intensity of the signal is higher in vacuum than in air. This behaviour has been ascribed[127] to oxidation of the dye by the bromine formed by photodecomposition of silver bromide: addition of bromine to dyed silver bromide in the dark does, in fact, induce a narrow EPR signal. The concentration of unpaired electrons on illumination is 10^{13}–10^{14} per 0.4 g silver bromide which has absorbed the dye from a 10^{-4} M solution.

Illumination of triphenylmethane dyes in a vacuum of 13.22 mN m^{-2} at room temperature produces a narrow signal which decays in the dark[128]. Admission of oxygen and quinone vapour suppresses the signal in some cases (Malachite Green, Crystal Violet), and increases it in others (Bengal Pink, Phloxin). This effect is entirely analogous to the effect of electron acceptors on the conductivity of dyes if we identify the current carriers with electrons in the former case and with positive holes in the latter.

These observations provide further confirmation of the generality of the causes of anomalous magnetic and electrical properties in compounds with conjugated double bonds.

§ However, the phthalocyanine was transferred from the sublimation apparatus to its container in the air: this could have caused partial oxidation.

V. ELECTRICAL PROPERTIES

Polymer with conjugated double bonds. As we stated above, polymers with conjugated double bonds have a fairly high electrical conductivity owing to the presence of a well-developed system of π conjugation and electron delocalisation. It should be noted that the π electrons in these polymers must have sufficient energy to permit tunnelling transitions through the intermolecular barrier if the electrical conductivity of the polymer is to have a significant magnitude [129]: thus, macromolecular orientation and structural effects play a significant role, as well as electron delocalisation, in determining the electrical properties of polymers.

The electrically conducting polymers first investigated were the products of the high-temperature pyrolysis of vinyl polymers [1,5,43,130-132]. The conductivity of the product increases with pyrolysis temperature: heating to 700° gives a value of $\sigma = 100$ μS m^{-1}¶, whereas $\sigma = 100$ S m^{-1} is obtained at 800°. The pyrolysis products have an extensive three-dimensional structure of six-membered rings, and a low hydrogen content (1–3%). They can be regarded as intermediate between linear polymers with conjugated bonds and products of carbonisation (coals, graphite). The electrical conductivity of the pyrolysis products of all vinyl polymers varies exponentially with temperature: $\sigma = \sigma_0 \exp(-\Delta E/2kT)$.

This relationship characterises all polymers with conjugated bonds, but it is nevertheless possible to classify these polymers into two groups according to their electrical properties.

Polymers of the first group have a structure consisting of condensed rings. Their electrical conductivity is high (1 mS m^{-1}–10 nS m^{-1}), and their forbidden gap is not very wide (< 0.08 aJ)†, which makes them very similar to inorganic semiconductors. One such "organic semiconductor" is pile irradiated or heat-treated polyethylene [52,133], in the temperature interval from -25° to +150°. An increase in integral radiation dose, or especically in the temperature of heat treatment, lowers the activation energy ΔE and increases the conductivity.

High electrical conductivity is found also in oxidised polyvinylene, heated in a vacuum [40] to 150°, and in the degradation product of poly(vinyl chloride) heated in air [134] to 400°. Condensed aromatic structures are apparently formed in both cases. Yet, when poly(vinyl chloride) is heated to 500° in a nitrogen atmosphere (*i. e.* without oxidative dehydrogenation) its electrical properties are close to those of an insulator [124].

The first group includes also heat-treated polyacrylonitrile [42,73], whose electrical conductivity at 20° ranges from 20 μS m^{-1} to 2 kS m^{-1}, with an activation energy of 0.037–0.125 aJ, depending on the temperature of heat-treatment [135]. The electrical conductivity of tetracyanethylene polymers is close to 0.1 μS m^{-1} at room temperature, and there is only one report [75] of its reaching 10 μS m^{-1}. The activation energy and the pre-exponential term depend on the type of polymerisation catalyst used.

The effect of oxygen on the electrical conductivity of these polymers is not unique. With heat treated polyethylene, oxygen increases the electrical conductivity of the system. However, beyond a certain temperature (which depends on the heat-treatment temperature) this relationship no longer applies [52]. Heat-treated polyacrylonitrile has an electrical conductivity showing a distinct "oxygen effect" [136,137]: after heating to 420° in a high vacuum, the electrical conductivity of the specimens increases by one order of magnitude, but it recovers its original value in the air. The smallest effect is observed in specimens heated to the highest temperatures (670–730°). At the same time, the thermoelectric power of the polymers becomes negative‡, whereas before heating *in vacuo* it was either negligible or large and positive. This effect is also reversible. The thermoelectric power of conducting polyethylene, on the other hand, increases in an oxygen atmosphere and remains positive [52].

The properties of semiconducting polymers can be altered also by treatment with halogens. Adsorption of iodine at 20° raises the electrical conductivity of "conducting" polyethylene by five powers of ten [138]. The temperature variation of the electrical conductivity of the polymer remains exponential from -80° to +20°, with a value of ΔE unchanged by the iodination. Above 125° the increase in conductivity stops, and on cooling the specimen a different temperature law is observed: this is probably characteristic of the product of the reaction between the polymer and iodine. The Seebeck coefficient of iodinated polyethylene is positive, and increases with temperature.

Adsorption of iodine in a vacuum at 240° increases both the electrical conductivity of polyethylene and the value of ΔE. At higher temperatures the conductivity type of the polymer changes. The manner in which the electrical properties of the polymer change with temperature corresponds to the transition from impurity conduction to intrinsic conduction observed in inorganic semiconductors. The value of ΔE calculated theoretically is in good agreement with the experimental value. It is assumed that iodine (and oxygen) can lower the potential barriers between the units taking part in multiple conjugation in the polymeric macromolecules, and thus raise the carrier mobility. This hypothesis is supported by the decrease in the "oxygen" and "iodine" effects in polymers having extensive structures following high-temperature treatment.

The thermoelectric properties of various polymeric nitriles have been studied as a function of temperature [137,139,140]. The Seebeck coefficient of polyacetonitrile and of a polymeric Schiff base decreases with increase in temperature, and changes sign. With paracyanogens and polyacrylonitriles this parameter is temperature-independent at first, and then begins to decrease.

The temperature at which the Seebeck coefficient of polyacrylonitrile changes sign varies from 120° to 425° according to the temperature of heat treatment. Thus, the conductivity type of semiconducting polymers at a given temperature can be varied. The current carriers are fully or partly degenerate, so that their concentration is not a function of temperature, and carrier mobility is the only factor which determines the change in electrical conduc-

¶ 1 S m^{-1} = 0.01 Ω^{-1} cm^{-1}, in accordance with the SI international system of units [However, British Standard 3763: 1964, "The International System (SI) Units" does not give a unit of conductivity. S is the abbreviation for Siemens (≡ A/V) and is the Continental term for the mho, or reciprocal ohm (Ed. of Translation).]

† 1 aJ = 10^{-18} J = 6.25 eV, or 1 eV = 0.16 aJ, in accordance with the SI international system of units.

‡ With the exception of the specimen heated at 730°, whose Seebeck coefficient, however, is extremely small (+0.7 μV deg^{-1}).

tivity of the polymers with temperature. The plot of the Seebeck coefficient of the polymers against the logarithm of their electrical conductivity does not agree with theory, because no allowance is made for the variation of carrier mobility with temperature of heat treatment.

Polymeric chloropyridine ($\sigma_{27°} = 10$ μS m^{-1}, $\Delta E =$ = 0.128 aJ)[95], and the polymeric condensation products of 2,6-lutidine with aromatic dialdehydes ($\sigma_{20°} = 30$ nS m^{-1})[61], have a fairly high electrical conductivity despite the fact that their structure is not cyclic. Aniline black should also be regarded as an organic semiconductor. The high conductivity of the material before alcohol-extraction is almost certainly due to impurities. However, the purified hydrochloride of aniline black is also electrically conducting ($\sigma_{27°} = 1$ mS m^{-1}; $\Delta E = 0.027$ aJ). Hydrochlorides have a significantly higher electrical conductivity than their bases[105]. We believe this to be due to the formation of ordered structures within the solid polymer: the number of such structures increases when the hydrochlorides are formed, because of the ionic bonds N^+Cl^-. When current is passed through the products of the oxidation of aromatic amines by sulphuric acid, an electromotive force is generated[65]. It is probably connected with the presence of ionised sulphonate groups in the polymers (sulphur content 3.83–16.23%). Materials of this type may find application in electrical storage cells[43].

We have seen that the most electrically conducting polymers with conjugated bonds contain nitrogen. This is not fortuitous: the presence of atoms whose outer electrons are relatively weakly bound lowers the activation energy and therefore facilitates the transfer of electrons to localised levels or to the conduction band[129].

The second group of polymers consists of those with linear or slightly branched structures, and having lower electrical conductivities (10 nS m^{-1}–10 fS m^{-1}). It includes, first of all, the polyvinylenes formed by thermal degradation of poly(vinyl bromide)[43], by dehydrochlorination of poly(vinyl chloride) by sodium pentyl oxide[40] or ultraviolet irradiation[31,32], and also the polymers of acetylene[11,12]. The electrical conductivity of these compounds is rapidly and appreciably decreased by the action of oxygen, from which they can never be completely freed. We include in this group the polyazines ($\sigma_{20°} = 0.1$ nS m^{-1}–0.1 fS m^{-1}; $\Delta E = 0.26$–0.45 aJ)[59], and the polymer of the malonodinitrile ($\sigma_{20°} = 2.3$ nS m^{-1}; $\Delta E = 0.163$ aJ)[76].

Tal'roze and coworkers[141,142] have measured the electrical conductivity at 20–80° of a large number of polymers with conjugated bonds — poly(phenylacetylene), its copolymers with hexene and *p*-diethynylbenzene, polyphenylene, poly(azophenylene)s, poly(aminoquinone)s — and have shown that ΔE varies linearly with $\log \sigma_0$ for all the polymers, in spite of large differences in σ_0 (0.1 nS m^{-1}–10^{10} TS m^{-1}) and ΔE (0.035–0.35 aJ). By analogy with known phenomena in chemical kinetics, this behaviour has been called the "compensation effect"[142]. All the polymers with broad EPR spectral lines were found to have a lower ΔE than required by the compensation effect, whence it was concluded that a correlation exists in general "not between the electrical conductivity and the EPR spectrum, but between the pseudoferromagnetic properties of the organic structures and their electrical conductivity"[142]. Since only the "pseudoferromagnetic" polymers definitely contained metal atoms, whereas the others were only assumed to contain such atoms, it would be more correct to speak of an increase in the electrical conductivity of polymers containing metals.

In polymers of the first group[71,135] the value of ΔE decreases with increase in σ_0, *i. e.* a compensation effect is not observed in general. It has been assumed[143] that this behaviour is common to all polymers with high electrical conductivity.

The electrical conductivity of poly-*p*-diethynylbenzene also does not exhibit the compensation effect[28], although $\sigma_{20°} = 0.1$–1 nS m^{-1}. Furthermore, the compensation effects occurs in typical polymeric dielectrics — such as polyethyleneterephthalate — when their electrical conductivity is lowered by increasing their degree of crystallinity[144]. The relationship $E = A + B \log \sigma_0$ holds for dielectrics as well as for polymers with conjugated bonds. The constant A takes the value 0.147 aJ and 0.106 aJ in the two cases respectively; $B = 0.5$ aJ in both cases. It seems clear that the compensation effect is characteristic only of polymers having a sufficiently high energy of intermolecular electronic transitions, but no explanation of this has as yet been given.

The introduction of methylene groups between the benzene rings of the polymer molecule causes a large decrease in the electrical conductivity of poly(azophenylene) and even polytriazene[84]. However, poly(azophenylene) "separated" by two methylene groups retains its high electrical conductivity[84,145]. According to Dulov *et al.*[145], the presence of one methylene group in the monomer unit of the polymer should also increase the conductivity, due to the denser molecular packings as compared with poly(azophenylene), which should facilitate intermolecular electronic transitions. The flexibility contributed by $-CH_2-$ groups permits close packing of the macromolecules. In the presence of two consecutive groups, however, the disturbance of the conjugation should predominate, and the electrical conductivity should decrease. The close juxtaposition of the polymer molecules probably accounts for the slight effect of thermal treatment upon its electrical conductivity: heat treatment of poly(azophenylene), on the other hand, causes a large increase in conductivity.

The electrical conductivity of poly-*p*-diethynylbenzene also increases when the material is heated in a stream of nitrogen[18] to 400–500° and 600°. Ultraviolet irradiation of the polymer after heating to 220° produces a large increase in conductivity, but after a 400° treatment the effect of irradiation is small, and after a 500° treatment the effect disappears.

The polymeric condensation products of polyhydric phenols with aromatic acid anhydrides have semiconducting properties[97]. Their electrical conductivity covers a large range of values. It depends on the nature of the constituents of the polymer, and increases with increase in polymerisation temperature (256–306°) and in compacting pressure (up to 0.98 GN m^{-2}). It usually lies between 1 and 100 μS m^{-1}, but in certain polymers it can reach 3 mS m^{-1}. Measurements of carrier concentration at -196° gave a value of $n = 10^{15}$ cm^{-3}. These polymers conduct mainly by positive holes.

Dyes. The semiconducting properties of phthalocyanines were discovered[146,147] in 1948. These would appear to be the earliest investigations of the electrical properties of compounds with conjugated double bonds. Subsequently, semiconductor properties were shown to be present also in diphenylpicrylhydrazyl[147] ($\Delta E = 0.04$ aJ), dyes of various classes[148,149] ($\Delta E = 0.16$–0.36 aJ), and blood pigments[150,151]. As in the case of polynuclear hydrocarbons, the width of the forbidden gap (ΔE) depends on

the purity of the material and on the atmosphere in which the measurements are conducted (see Table). The slight increase in the activation energy of phthalocyanine in oxygen is due to surface oxidation, which increases the height of the energy barriers between microcrystallites.

The dark conductivity of phthalocyanines at room temperature is less than 0.1 nS m^{-1}.

Semiconducting dyes show appreciable photoconductivity[154]. As in the case of the dark conductivity, the magnitude of the photocurrent increases in an oxygen atmosphere and on raising the temperature. The activation energy attending photoconduction in these dyes is[152] 0.06–0.10 aJ, which is not very different from the energy of singlet–singlet transition[155]. On the other hand, the photocurrent in basic dyes (with the exception of Trypaflavine) decreases in an atmosphere of oxygen or water vapour[156].

The sign of the current carriers in semiconducting dyes were determined by a variety of methods[156,157]. Electronic conduction was found in di- and tri-phenylmethane dyes, and in some xanthene and cyanine dyes; the conduction in the other dyes, including phthalocyanines, was by positive holes. Yet the Hall constant of "metal-free" phthalocyanine is negative[153]. The carrier density (obviously, electrons) in this material is 10^6–10^7 cm^{-3}.

Since the crystal contained 0.02–0.2% of copper, one is forced to the conclusion that metal impurities are practically without effect on the electrical conductivity of phthalocyanine.

The mechanism of conduction in organic dyes involves electron capture at localised energy levels, from which the electrons can be emitted into the conduction band (or recombine with holes in the case of *p*-type conduction)[156].

VI. ABSORPTION SPECTRA

The absorption spectra of dyes have been studied and described in great detail[8]. We shall therefore confine our discussion to the absorption spectra of polymers with conjugated double bonds.

The infrared spectrum of polyvinylene, prepared by treating poly(vinyl chloride) with potassium amide, contains bands which are typical of *trans*-vinylene groups,

TABLE. Semiconductor properties of porphyrin compounds.

Compound	Temperature range, °K	ΔE, aJ		Reference
		in vacuo	in oxygen	
Phthalocyanine	273–373	0.139	0.142	146
	373–773	—	0.38	147
	423–623	0.24	—	147
Phthalocyanine under 7.85 MN m^{-2} pressure	398–543	—	0.13	147
	543–673	—	0.18	147
α-Phthalocyanine	323–443	0.04	—	116
β-Phthalocyanine	573–673	0.14	—	116
Phthalocyanine	293–473	0.27	0.30	152
	—	0.27	—	153
Sulphonated phthalocyanine	273–373	0.144	0.147	146
Hematin	345–403	0.29	—	149
	123	0.325	0.325	151
Hemoglobin	373–423	0.44	—	150
Globin	373–423	0.475	—	150
Hematoporphyrin	—	0.331	0.336	151
Protoporphyrin	—	0.29	—	151

and also a weak band at 1170–1150 cm^{-1}, corresponding to oxygen bridges between the macromolecules[158]. This band is drastically suppressed by oxidation of the polymer: at the same time, typical bands for the OH and C=O groups appear, and a strong absorption (due to the formation of a network of C–C– and C–O–C bonds) is observed in the region 1000–1300 cm^{-1}. A strong absorption at ~1300 cm^{-1} occurs also in the polymeric condensation product of acetaldehyde[50], in poly(azophenylene), and in poly(phenylacetylene)[159]. With the latter polymer the background absorption increases as the depth of colour of the material increases, the characteristic bands in the 700–1800 cm^{-1} region decreasing in intensity at the same time. In the infrared spectra of the copolymers of poly(azophenylene) with *p*-diethynylbenzene, and also in those of poly-*p*-diethynylbenzene, the characteristic absorption bands are either very weak or quite unresolved; the background absorption in these spectra is very strong over the whole frequency range[159]. The infrared absorption spectra of other polymers with conjugated bonds show only some well-defined functional groups[53,55,83]. A systematic survey[160] of the infrared spectra of various polymers with conjugated bonds has shown that an appreciable absorption band is always present at 1585 cm^{-1}, and is stronger than the 1615 cm^{-1} band. It is due to the appearance of a quinonoid structure in the polymer as a result of conjugation. The introduction of substituents in the benzene rings, and also the presence of intermediate groups such as triazene or methylene groups, decreases the proportion of quinonoid structures in the polymers.

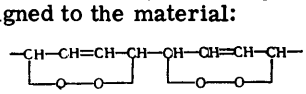
Some bands were also found to correspond to stretching vibrations of the carbon–carbon bonds between benzene rings: these disappear when the system departs from coplanarity. The insoluble polymeric fractions had a stronger background absorption, and less well-defined characteristic absorption bands, than the soluble fractions. This can be attributed to the strong intermolecular interaction between conjugated polymer chains. The strong background absorption of three-dimensional polymers with an extended system of conjugation was again confirmed.

Absorption spectra in the visible region were obtained only with irradiated poly(vinyl chloride)[33]. Under the influence of fast electrons (whether in vacuum or in air) a colourless film of the material develops a green colour with an absorption maximum in the region 580–700 nm. At the same time, an absorption peak develops at 420–460 nm, its intensity depending on the integral dose of radiation. When irradiated poly(vinyl chloride) is kept in a vacuum, the absorption curve shifts towards the visible region without changing shape; the transmission coefficient of the film initially decreases at $\lambda > 560$ nm, and then begins to increase in the region of 500–760 nm. There are no definite conclusions regarding the origin of these phenomena.

VII. REACTIVITY

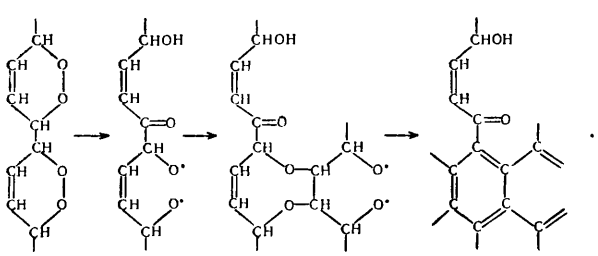
Polymers with conjugated double bonds. As a rule, high-molecular polymerisation products with conjugated double bonds do not show a pronounced tendency to react chemically: they are stable towards atmospheric oxygen at 200–250°, and [polyphenylenes and poly(oxyphenylene)s] even up to 400°.[161] Other oxidising agents are also without effect. Poly(aminoquinone)s have a tendency to form chelates with copper and other metallic salts, but this specific property can be ascribed[53,55] to the presence of the >NH group.

Polymers of the polyvinylene type occupy a unique position. Polyacetylenes are easily oxidised by benzoyl hydroperoxide; the resulting peroxide is hydrolysed and oxidised by lead tetraacetate to carboxylic acids[10]. Chlorination of the polymers gives a white insoluble product containing 40% of chlorine[14]. The product of full dehydrochlorination of poly(vinyl chloride) is easily oxidised in the air[39,40], changing from black to light yellow. Meanwhile, its oxygen content increases, the composition changing from $CH_{1.12}O_{0.11}$ before oxidation[41] to $CH_{1.12}O_{0.4}$. According to the degree of dehydrochlorination (0.63–92.91%), the amount of oxygen absorbed varies[162] from 1.65 to 30.32%. It has been stated[40] that oxidised polyene contains up to 32.5% of bound oxygen as well as double bonds; in view of the *trans*-configuration of neighbouring vinylene groups, the 1,4-peroxide structure is assigned to the material:



Oxidation of the polymer obtained from poly(vinylidene chloride) proceeds in a similar way. In every case oxidation causes the loss of the EPR signal and lowers the conductivity of the polymers.

The compound between polyvinylene and oxygen is fairly stable, since it does not decompose in air, but it shows a loss in weight at 150° and above[40]. Boiling 30% nitric acid partly dissolves the product, with formation of oxalic acid and carbon dioxide. The oxidised polymer does not react with potassium iodide, and does not respond to any test for peroxide[162]. When heated in vacuum at 200°, the product gives CO_2, water, alcohols, and phenols, with loss of 50% of the bound oxygen; the resulting new polymer is stable to oxidation at high temperatures and gives an EPR signal, and its conductivity is higher by two orders of magnitude[40]. Its melting range[41] is 400–410°. It is suggested[163] that when the peroxide is heated in the absence of oxygen, rupture of the peroxide bridges takes place, followed by polymeric condensation and formation of aromatic structures by partial degradation of the polymer:



The peroxide of polyvinylene oxidises tetralin to decalin[40] at 150° in an inert atmosphere. It can induce the polymerisation of methyl methacrylate even at concentrations of 0.1–0.5 wt.% in the monomer[182].

No significant oxygen affinity could be detected in poly(phenylacetylene), yet it is formed in higher yield in air than in an inert gas[19]. It does not react with maleic anhydride and, like polyacetylene, it is sluggishly hydrogenated by Raney nickel supported on alumina[10]. However, the properties of the polymer are dramatically changed by heat treatment at 300–400° in oxygen or argon: the material darkens and becomes black, it becomes insoluble in acetone and stable to oxidation at 200–300°, its EPR signal increases, and it develops static paramagnetism (the polymer prepared at 150° is diamagnetic). The reaction between poly(phenylacetylene) and *p*-diethynylbenzene at 150° gives a black, insoluble polymer having a three-dimensional structure, as in the case of phenylacetylene[19]. This type of copolymerisation has been called[164] "quasi-radical block copolymerisation"; it appears to occur exclusively with polymers having conjugated bonds. The radiation-induced polymerisation of phenylacetylene is also unusual[26]: its rate is proportional to the integral dose of radiation between wide limits, is independent of dose rate, and is relatively insensitive to temperature (E = 0.005 aJ). The activation energy for initiation is zero. Lastly, poly(phenylacetylene) inhibits the degradation of poly(vinyl chloride)[165] by thermal oxidation at 175–195°, in the same way as (but much more effectively than) compounds which readily yield free radicals. Polyvinylenes have a weaker inhibition effect: at 195–200° they accelerate the degradation of the polymer rather than inhibit it[166]. Polyphenylenes and poly(azophenylene)s do not show an inhibition effect at 175°: the effect appears only[163] at 195–200°.

All four polymers decrease the photochemical aftereffect of the oxidative degradation of poly(vinyl chloride) (leading to the formation of regions with conjugated double bonds and, ultimately, to a polymer of the polyvinylene type).

All the properties listed above justify the conclusion that polyvinylenes, polyphenylenes, and poly(azophenylene)s are free radicals whose relative stability arises from their large size and the strong delocalisation of the free electrons in the macromolecule: they have been termed radicaloids[80,163]. The additional withdrawal of the π electrons by the side-chains of benzene rings explains the higher stability of poly(arylacetylene) radicaloids as compared with polyvinylene. The radicaloids become activated at 200–250°, and undergo "quasi-radical" polymerisation and copolymerisation. The radicaloids combine with oxygen, and thus inhibit the degradation of poly(vinyl chloride), but at some stage in the process they become oxygen carriers and begin to accelerate the degradation.

The higher yield of polymer in oxygen is probably also due to the formation of intermediate, very active compounds between the radicaloid and oxygen: this type of "oxygen activation" has also been observed during the radiation-induced polymerisation of phenylacetylene[23], but its activating effect is much smaller than that of radiation.

The small degree of polymerisation of acetylene hydrocarbons is explained by the process of chain propagation through the monomer, which is peculiar to these materials, giving rise to R–C≡C$^{\bullet}$ (M$^{\bullet}$) radicals which do not regenerate the chain and disappear.

This "autoinhibition" mechanism is equally applicable to radiation polymerisation and to thermal polymerisation, initiated by benzoyl peroxide[167,168]. It can be described by the following kinetic schemes:

Type of process	Radiation polymerisation	Polymerisation initiated by benzoyl peroxide (B)
Chain generation	$M \xrightarrow{k_0} 2R^{\bullet}$	$M + B \xrightarrow{k_0} R^{\bullet} + B^{\bullet}$
Chain growth	$R^{\bullet} + M \xrightarrow{k_1} R^{\bullet}$	$R^{\bullet} + M \xrightarrow{k_1} R^{\bullet}$
Chain propagation and breaking	$R^{\bullet} + M \xrightarrow{k_2} RH + M^{\bullet}$	$R^{\bullet} + M \xrightarrow{k_2} RH + M^{\bullet}$ $B^{\bullet} + M \xrightarrow{k_3} BH + M^{\bullet}$
Recombination	$M^{\bullet} + M \xrightarrow{k_3} D$	$M^{\bullet} + M \xrightarrow{k_4} D$

The rates of radiation and thermal polymerisation, W_R and W_T, are given by the expressions

$$W_R = \left(3 + \frac{2k_1}{k_2}\right) k_0 I [M],$$

$$W_T = \left(2 + \frac{k_1}{k_2}\right) k_0 [M][B],$$

and are therefore proportional to the dose of radiation or to the concentration of initiator. The value of k_1/k_2 is the same in both cases (3.5–4.0).

Polyazines[59] differ from poly(azophenylene)s in being much less stable at high temperatures; they all melt or decompose at 210–270°. Poly(azinoglyoxal) decomposes explosively, losing 67.5% of its original weight, with evolution of nitrogen, hydrogen, amines, and hydrocarbons. The solid residue is infusible and has a much higher electrical conductivity, and is therefore thought to consist of polyvinylene:

$$(=CH-CH=N-N=)_x \longrightarrow xN_2 + (-CH=CH-)_x.$$

The low thermal stability of polyazine stems from the large number of azo-groups and of partially aliphatic groups in the chain, instead of aromatic groups.

In contrast to the low-molecular polyazophenylenes with CH_2 groups in the conjugated chain[84], poly(phenylmethylene)s, produced by different methods[87-99], have a molecular weight $M > 20\,000$, and do not show any "quasi-radical" properties. Relatively low molecular weights (M = 1000–1300) are found in certain poly(naphthylmethylene)s; it is significant that the material with the highest molecular weight (M = 5800) proved to be diamagnetic[93].

The direct reaction of poly(phenylacetylene)s, polyphenylenes, and poly(azophenylene)s with diphenylpicrylhydrazyl (DPPH) suppresses the EPR signal of the latter without affecting the signal of the polymer[169]. The reaction of the first order with respect to the polymer, second order with respect to DPPH, and its product is[170] DPPH-H. The hydrogen is extracted from a molecule of the polymer. The process is induced by paramagnetic centres, which do not themselves participate in the reaction. The fact that the EPR signal of polycyclopentadiene does not change when the material is allowed to stand for 24 h in a solution of 2,4,6-t-butylphenoxyl in a nitrogen atmosphere[107] may be a phenomenon of the same type (but the final concentration of 2,4,6-t-butylphenoxyl was not evaluated).

Polymerisation by the "quasi-radical" mechanism produces three-dimensional high-molecular polymers. Their insolubility in organic solvents, and their stability towards oxidative thermal degradation, in conjunction with their high concentration of unpaired electrons and their static paramagnetism, suggest that the cyclic structure of these materials has the form of a network of aromatic rings which is typical of carbon blacks and coals. The great practical importance of "quasi-radical" reactions by polymers with conjugated double bonds will undoubtedly stimulate further work in this field.

By analogy with inorganic semiconductors, certain polymers with conjugated double bonds may be expected to show catalytic activity, since they are organic semiconductors. The decomposition of hydrogen peroxide is, in fact, accelerated by the presence of aniline black[105], poly(aminoquinone)s[171], and polyacrylonitrile[73]. In the first two cases, the catalytic activity can hardly be ascribed to the organic structure itself, particularly since these polymers have a wide EPR signal and the activity of aniline black decreases with decrease in the chromium content. Furthermore, hydrogen peroxide is extremely sensitive to the catalytic effect of a great variety of solids, and it is difficult to relate these results uniquely to the electronic properties of organic semiconductors[172].

The oxidation of formic acid on polyacrylonitrile[172], whose catalytic activity reaches a steady-state value only after four consecutive experiments, gave more revealing results. The decomposition goes preferentially in the direction of formation of hydrogen. A polymer containing 0.01% of copper(II) chloride is slightly more active (E = = 0.148 aJ; for the copper-free polymer E = 0.176 aJ). Polyacrylonitrile does not catalyse the decomposition of alcohols or the hydrogenation of ethylene.

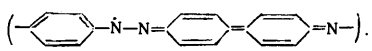
There are some data on the catalytic properties of polyvinylenes. Thus, the polymer of 2-chlorovinyl methyl ketone, when heated to 400° at 1600 N m^{-2}, catalyses the oxidation of toluene by air at 380° as effectively as activated carbon with a surface area 2000 times greater[47]. The oxidation proceeds much more smoothly than on transition metal oxides. Again, the polymer containing iron(III) chloride added as an initiator was found to be much more active than the "metal-free" polymer. The same product heated to 1000°, and poly-*p*-diethynylbenzene, heated to 500° or 600° (all in a nitrogen atmosphere), accelerate the conversion[173] of *o*-H_2 into *p*-H_2. It has been suggested that the active regions of the surface of these polymers can be identified with paramagnetic centres, also the catalytic activity does not vary symbathically with the paramagnetism of the material: only the least active catalyst (poly-*p*-diethynylbenzene heated to 500°) gives an EPR signal. The polymer heated to 600° catalyses the decomposition of formic acid. This property has also been observed in polyvinylene prepared with potassium amide[174] and having the composition $CH_{0.68}N_{0.13}O_{0.14}$. However, the two sets of phenomena are radically different. Hydrogen is sorbed on poly-*p*-diethynylbenzene slowly and weakly, but it is chemisorbed on polyvinylene, which gradually decreases the reaction rate. The chemisorbed hydrogen is only partly removed at 400°. Polyvinylene catalyses also the dehydrogenation of propan-2-ol and the decomposition of hydrazine into nitrogen and ammonia; these processes as well are characterised by considerable sorption (of hydrogen in the former case, and of ammonia and hydrazine in the latter)[174]. As regards the decomposition of hydrazine, it is difficult to speak of a catalytic effect of the polymer, since the reaction occurs above 250°, and both the homogeneous decomposition and the reaction at the glass walls become significant at these temperatures. This is also true of the effect on polyacrylonitrile[172]. The catalytic properties of polyvinylenes can be explained in terms of the formation of intermediate addition compounds at the double bond. However, polyvinylene prepared in an inert atmosphere does not catalyse the oxidation of alkylbenzenes[134] and of carbon monoxide[174], whereas polyvinylene prepared by heating poly(vinyl chloride) in air at 400° (and probably having a condensed structure) is a powerful catalyst for the oxidation of cumene and ethylbenzene[134]. Oxygen addition is probably responsible, giving compounds even less stable than peroxides.

VIII. THEORY

The theory underlying the properties of compounds with conjugated double bonds presents a difficult problem, which has not yet been finally resolved. Qualitative ideas on the

fundamental role of π electrons free to move along the entire length of the conjugated chain [1-3], although correct, are obviously inadequate: they cannot explain, for example, why the number of unpaired electrons is always less than the number of molecules and yet the diamagnetic fractions in certain polymers [163] amount to 90%.

Some discussion is needed of the possibility of π conjugation in polymers containing benzene rings separated by $-CH_2-$ groups. It has a low probability, since the π electron has to overcome an energy barrier of 0.96-1.12 aJ. It has been shown [175] that spin exchange occurs in the dibenzyl anion, preventing isomerisation with formation of a conjugated chain [176]. However, anion-radicals, which are equilibrium species with one unpaired electron per molecule, and solid polymers, consisting of macromolecules which are diamagnetic in their ground state, are hardly comparable. Polyphenylmethylenes are colourless, have a high molecular weight and a low softening point, and show static diamagnetism: thus, they cannot belong to the class of polymers with conjugated double bonds. Statements [84,145] that electron delocalisation occurs in poly(azophenylmethylene)s are incorrect. The EPR signals of these materials, their high electrical conductivity, and other anomalous properties, can be explained merely by the presence of nitrogen atoms with a tendency to form quinonoid groups of the type



The flexibility of macromolecules containing CH_2 groups could be a factor contributing to the electrical conductivity of poly(azophenylmethylene)s [145].

We have at the moment three basic hypotheses on the nature of the magnetic and electrical properties of compounds with conjugated double bonds. According to the first of these [120,122], these properties stem from the paramagnetic impurities which are invariably present in compounds of this type. It has also been stated [163] that dyes and polynuclear hydrocarbons should not be treated as monomeric compounds, because their properties depend on the amount of high-molecular product present in the material. This hypothesis is unsatisfactory, because it fails to explain why the high-molecular impurity should be paramagnetic (paramagnetic ion impurities are excluded, because they can be easily removed), nor does it explain why the impurity is so strongly bound to the host material that it sometimes cannot be removed even by repeated purifications, or why the diamagnetic major constituent is prone to "quasi-radical polymerisation"§.

Another hypothesis aims to interpret compounds with conjugated bonds as charge-transfer complexes (c.t.c.), similar to the complexes formed between benzene and iodine, etc. The c.t.c. concept was first extended to polymeric systems by Blyumenfel'd and Benderskii [177], who showed that a donor-acceptor complex is stable as a linear chain with alternating charges. At the same time, the value of the exchange integral increases with the number of conjugated bonds, giving rise effectively to a single molecular orbital. However, the authors ascribe the ionised states in polymers to the existence of "regions of structural order".

§ The assumption of long-lived macro-radicals is refuted by the EPR signal and the "quasi-radical" polymerisation observed in the formation of the primary polymer by an ionic mechanism, and by the failure of poly(cyclopentadiene) to react with tri-t-butylphenoxyl.

These ideas have been developed in greater detail [178]. The electrical and magnetic properties of systems with conjugated bonds are determined by c.t.c., which are formed either between molecules or between conjugated units within a molecule. It is incorrect to ascribe these properties to the proximity of ground and lowest excited states, resulting from the decrease in activation energy accompanying an increase in the length of the conjugated chain, since this mechanism does not operate at any chain length. The preferential formation of c.t.c. between conjugated systems is due to the fact that the distance between the components of the c.t.c. is less than the distance between neutral molecules. When the material is crystallised, the number of polar states is a maximum at the phase boundary, and as a result the number of c.t.c. in crystals is much larger than in solution. Thus, we can think of these complexes as growth dislocations inevitably arising during crystallisation; it follows that the transition from c.t.c. to a neutral state is impossible without considerable rearrangement of the crystal.

The electrical conductivity of systems with conjugated bonds [178] is explained in terms of the dissociation of c.t.c., charge carriers being set free. The motion of conduction electrons in molecular crystals is accompanied by an adiabatic wave of electronic polarisation, leading to a decrease in the intrinsic energy of the electron. The polarisation energy is given by the expression

$$E = -\frac{D}{V_0} K_{nn} \sum_i \frac{f_i}{\epsilon_i^2},$$

where D is a coefficient depending on crystal geometry, V_0 the volume of one molecule in the crystal, K_{nn} the coulomb integral for two electrons in the upper filled orbital, f_i the oscillator strength, and ϵ_i is the energy of the excited states.

The fact that identical activation energies have been observed [155] for the dark conductivity, the photocurrent, and the first singlet state of a number of dyes justifies the suggestion that excitons with an energy of formation equal to the singlet-singlet transition energy can arise in compounds with conjugated bonds. According to Benderskii and Blyumenfel'd [178], exciton formation is possible when the number of c.t.c. exceeds 10^{16} cm^{-3}. When this happens, the electrical conductivity of conjugated systems can increase as a result of the capture of electrons by localised levels lying above the valence band, accompanying the dissociation of the excitons.

It should be stressed that the exciton conduction mechanism is hardly ever encountered in dyes [129].

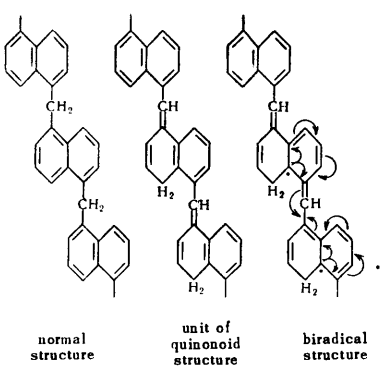
The c.t.c. hypothesis explains also the conductivity of polymers with conjugated bonds. Although the π electrons are sufficiently mobile within the macromolecule, electrical conductivity of the material as a whole requires that the electrons cross the potential barrier between macromolecules. This process is made much easier by the existence of intermolecular c.t.c.

The c.t.c. hypothesis is acceptable only for dyes in which the EPR signal is observed exclusively in the solid phase. The increase in strength of the EPR signal of polycyclopentadiene in air can only be explained by the formation of c.t.c. with oxygen, which acts as a charge acceptor. A c.t.c. with oxygen may also be formed at the surface of cyclic polyvinylene [134]; the existence of O_2^- radical-ions as a surface layer on the polymer may be another limiting

case of charge transfer. The reversible increase in EPR signal accompanying decrease in temperature (by Curie's law) is consistent with c.t.c. concepts.

By combining the c.t.c. and the radicaloid hypotheses we arrive at the concept of "local activation" of polymers with conjugated double bonds, according to which high--molecular, paramagnetic polymeric homologues form π complexes with the main bulk of the macromolecules, which then activate the system as a whole [163]. The formation of c.t.c. of this type increases the probability of excitation of diamagnetic macromolecules to the biradical state. This model provides a satisfactory explanation of the processes of "quasi-radical" polymerisation and of hydrogen transfer from the polymer of DPPH. The paramagnetism of the high-molecular fractions arises [163] from local unpairing of electrons, and from electron delocalisation along the molecule due to the close proximity of filled and unfilled energy levels. The existence of stable unpaired electrons is made possible by the departure from coplanarity of the conjugated units of the macromolecule.

The hypothesis of electron delocalisation along the whole length of the conjugated chain has not found general acceptance. A theoretical analysis by the molecular orbital method [179] of the "charge density along the bond" in a long polyene chain has given a value of 30% for the delocalisation. The region of delocalisation in the poly(phenylacetylene) anion is confined to two units [180], and the same result was found by analysing the shape of the EPR line of solid poly(phenylacetylene) [181]. Ooshika [182] has reported limited distribution of electrons in an infinitely long chain, and regular alternation of bonds. As a result, he suggests that some particular units in the polymer chain have the nature of free radicals and show appreciable electron delocalisation. In contrast to "structural ordering", these units should be regarded as defects in the polymer chain. The tautomeric forms ascribed [93] to paramagnetic poly-(naphthylmethylene)s are an example of such units:



These "defect sections" are always possible in polyene chains of sufficient length owing to perturbation of the regular alternation of single and double bonds [183]. They can be caused by thermal vibrations, since the energy of formation of the defects is 0.035 aJ. At 300°K they are present in the molecule to the extent of 1.4% by concentration. The defects can move rapidly along the molecule, and become the site of an unpaired electron when they are at a sufficient distance from other similar defects. Defects in the polymer chain can enhance its semiconductivity, since thermally excited electrons are more readily transferred to "defect" orbitals than to the conduction band.

Levich *et al.* [184] state that the conductivity of a polymeric molecule (considered as a one-dimensional conductor with degenerate electrons) is determined by the interactions between electrons and "defects", and is independent of temperature. However, the width of the EPR line is determined by the spin interaction of the electron with the nuclei of atoms in the polymer.

It is not possible at the present time to choose between the hypotheses discussed above. A theory of the properties of compounds with conjugated double bonds which shall be free from contradictions must await new, detailed, and careful investigations.

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PRESENT-DAY METHODS OF SYNTHESISING MACROCYCLIC COMPOUNDS

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1. INTRODUCTION

During the past 10–15 years the chemistry of macrocyclic compounds has been transformed from a relatively little studied section of organic chemistry into one of its most vigorously developing branches. The progress achieved by the present time is shown in the creation of new methods of synthesising macrocycles, the study of the specific physical and chemical properties of the simplest members of this class of compounds, and the investigation of complex natural products containing large and medium rings† as structural units.

The study of macrocyclic compounds is of considerable interest in the theory of organic chemistry. Compounds of this type exhibit very clearly the effect of various steric factors on physical properties and chemical behaviour. In virtue of the peculiar "compactness" of many-membered rings, especially those of medium size, substituents which are not directly linked together prove to be contiguous in space, and opportunities are created for the interaction of atoms and groups located on opposite sides of the ring (transannular effect). The investigation of macrocylic compounds has substantially extended and deepened our ideas on strain in rings and has revealed interesting information on the relation between the strain in and the reactivity of a ring. Finally, the study of the molecular structure of macrocyclic compounds, by such methods as X-ray structural analysis, infrared spectroscopy, and measurement of dipole moments, has given extremely valuable information on the relative arrangement of atoms in a many-membered cyclic molecule. These results together with calculations of the energetically most favourable conformations by the use of electronic computers will undoubtedly lead to the further development of conformational analysis in the immediate future. More detailed accounts of the above questions will be found in review papers[2-4].

Quite recently, in connection with the synthesis of the cyclic system termed a catenane, in which two rings are combined as links in a chain[5,6], most interesting questions have been posed concerning new forms of isomerism in macrocyclic compounds, solution of which will require

† At the present time macrocyclic compounds comprise those containing medium rings (8–12 atoms) and large rings (13 and more atoms). Small rings (containing 3 and 4 members) and normal rings (5-, 6-, and 7-membered) are combined into groups of so-called "classical" rings[1].

application of the elements of topology. These investigations will undoubtedly give an impetus to the further development of our seemingly established views of the molecule, since in a catenane the two rings are combined, not by a chemical bond, but "mechanically" as it were, and it still remains an open question whether the catenane system should be regarded as one or two molecules.

On the other hand, investigation of natural products has revealed the important biological role of macrocyclic compounds. Not long ago, physiologically active macrocyclic compounds comprised only a few alkaloids, porphyrins, and some perfumes; at the present time a large and ever increasing number of natural macrocyclic compounds are known with a clearly marked physiological activity (see for example Refs 7–14). Many alkaloids, for example tubocurarin, such hormones as oxytocin and insulin, and antibiotics, *e.g.* macrolides, gramicidin S, enniatin, valinomycin, etc., are macrocyclic compounds. It may be supposed that in many cases a macrocyclic structure is a necessary precondition for the presence of a biological effect. In this connection, work on the synthesis of macrocyclic compounds of potential biological activity has begun to be intensively developed. Among macrocyclic compounds which have been synthesised are substances having a curarelike[15], anticholinergic[16], and hypotensive action[17], analgesics[18], anaesthetics[19], and also weed-killers[20], insecticides[21,22], and growth promoters[22].

From what has been said it is clear that the development of new methods for synthesising macrocyclic compounds is an extremely urgent task. Many papers have been published on the preparation of macrocyclic compounds, their number growing continually and probably amounting at the present time to many hundreds. Without aiming at an exhaustive survey, we intend to systematise the most important achievements in the synthesis of macrocyclic systems‡, and refer the reader to Ziegler's fundamental review[23] published in 1955, which covers the literature up to September 1953. Here we shall be concerned mainly with more recent literature, referring to the earlier work only when necessary to make the exposition complete. The history of the chemistry of macrocyclic compounds will not be discussed, since a very detailed literature already exists on this topic (see in particular Refs. 24 and 25).

In my view the extensive literature on the synthesis of macrocyclic compounds can usefully be classified according to the type of reaction resulting in formation of a many-membered ring rather than according to the class of compound formed. The various reactions leading to the formation of macrocycles can be grouped in four fundamentally different types — (1) cyclisation, (2) depolymerisation, (3) syntheses involving a transannular bond, and (4) ring enlargement and contraction.

2. METHODS OF CYCLISATION

Macrocyclic systems have hitherto been obtained most frequently by the cyclisation of long-chain bifunctional compounds. The synthetic chemist now has at his disposal various methods of cyclisation enabling him to obtain acceptable yields of the most diverse macrocyclic systems. the chief obstacles to be overcome occurring quite frequently in the synthesis of the initial long-chain compounds and not in the process of cyclisation. However, ring-closure of the macrocycle itself is associated with several specific difficulties, which emerge more or less strongly with all methods of cyclisation. Before passing to an account of individual methods of cyclisation, therefore, let us examine some of the thermodynamic and kinetic factors which control the process, as well as the structural features of bifunctional compounds which facilitate cyclisation.

The difficulties associated with the preparation of macrocyclic compounds by processes of cyclisation are due to the low probability that the ends of a long chain will meet[26]. The tendency to ring formation is a complex function of the distance between the reactant groups and the loss of entropy associated with its fixation, the Baeyer strain, the Pitzer strain, and the contraction of the van der Waals radii[3,4].

Two reactions — intramolecular (ring formation) and intermolecular (polycondensation or polymerisation) — are in competition during cyclisation. In all cases other than the formation of five- and six-membered rings, the intermolecular reaction is thermodynamically the more advantageous[27,28]. However, the possibility of cyclisation is determined not only by thermodynamic but also by kinetic factors. Macrocyclic compounds, which were originally obtained in very low yields[29], can now be synthesised in quite high yields (see below and also the review in Ref. 23)§. This is achieved primarily by the use of high dilutions during cyclisation. The principle of high dilution, proposed by Ruggli[30], was first applied by Ziegler[31]. Under these conditions opportunities for intermolecular reaction are limited, while intramolecular cyclisation becomes more probable.

Apart from dilution, ease of cyclisation is affected by various structural factors which make more or less probable the occurrence of chain conformations which are convenient for cyclisation. For example, replacement of a methylene group in a bifunctional compound by oxygen usually results in an increased yield of the cyclic compound (the "oxygen effect" [23,32-34]), which can be explained by a diminution in conformational strain on substitution of a quadrivalent by a bivalent atom. The presence of rigid groups (multiple bonds, aromatic rings) in the chain of the compound to be cyclised decreases the mobility of the chain, and hence also the total number of possible conformations, so that favourable conformations become more probable and the yield of the macrocyclic compound is increased ("the rigid group principle" [23,25,35])¶. Ease of cyclisation can depend not only on ring size but also on whether the number of cyclic atoms is odd or even, since in several cases formation of a "coiled" chain with its ends close together, and not containing thermodynamically unfavourable

‡ The review does not cover inorganic macrocyclic compounds such as the cyclic siloxanes and phosphonitriles: it is confined to carbocyclic and "normal" heterocyclic compounds, the latter containing oxygen, sulphur, or nitrogen as hetero-atom.

§ Nevertheless, it must be remembered that compounds having medium rings, in which so-called "non-classical" strain is inherent[3], are obtained in lower yields, whatever the method of cyclisation used, than the strainfree compounds having large rings (*e.g.* Ref. 23).

¶ This statement concerning the influence of rigid groups relates, of course, to the synthesis of macrocyclic systems, but is not applicable to the formation of compounds containing normal rings.

eclipsed conformations, is possible only with chains having an odd number of members[34,36].

The probability of cyclisation can be increased by the presence in a bifunctional compound of even short substituent side-groups, restricting internal rotation. As a result, the chain can more often adopt "coiled" conformations with the functional groups close together and favouring cyclisation[34,37,38].

The influence of substituents on cyclisation is especially clearly developed in the synthesis of rings of medium size (8–12-membered)[39,40]. The presence of substituents plays an important part also in the preparation of small and normal rings. The opinion has even been expressed[41] that in general "the presence of substituents and their nature are of greater significance for the ease of formation and the stability of a ring than is the number of atoms in the ring alone".

In general it can be stated that the increase in rate of cyclisation accompanying introduction of substituents is caused primarily by the conformational effect[42]. Substituents favour an increase in the content of the gauche form at the expense of the transoid form, as a result of which the reactant groups occupy positions in which cyclisation is possible. More simply, if it is accepted[34] that the most favourable form for a polymethylene chain is a planar zigzag in which the ends of the chain (the functional groups) are as remote as possible from one another, substituents when present may become involved in the zigzag, and bring the functional groups closer together.

When the chain of a bifunctional compound contains several substituents, the compound usually contains several asymmetric atoms. In such cases the probability of the occurrence of a conformation convenient for cyclisation may be determined also by the steric configuration of its individual sections: in other words diastereoisomers may differ markedly in their capacity for cyclisation[43].

Bulky substituents near reactant groups may increase the probability of cyclisation not only by their effect on the conformation of the chain but also because they create steric hindrance to the intermolecular reaction. In fact, the use of bifunctional compounds containing large substituents makes it possible in several cases to obtain macrocycles without the employment of high dilutions[44,45].

The greater or lesser probability of the production of a favourable form of the chain will depend also on the mechanism of cyclisation. Thus in the acyloin condensation of dicarboxylic esters, which is carried out in heterogeneous medium, the probability of the alkoxycarbonyl groups coming together is increased by chemisorption on the surface of fused metallic sodium[32,46].

Let us examine some problems associated with the practical application of the high dilution principle. As noted above, the competing polymerisation or polycondensation is suppressed to a greater extent the lower the concentration of the cyclisable substance. In order to avoid increasing unduly the volume of the reaction mixture, this substance is usually introduced slowly into a moderate quantity of solvent containing a condensing agent or present under conditions (temperature, illumination, etc.) to ensure the occurrence of the reaction. In many cases the solvent is kept boiling vigorously, the condensate being used to dilute the substance undergoing cyclisation; the latter is therefore introduced into the reaction space in very dilute form, and thus the possibility of a local increase in concentration is excluded ("high dilution technique")†. Thus, instead of increasing the volume we increase the duration of the process.

In a chemical reaction which is carried on for a long time a point can be reached at which as much reactant enters the reaction zone in unit time as is removed from it by the reaction. Actually, if reactant is supplied at a constant rate $(dc/dt)_f$, while its rate of consumption is $-(dc/dt)_r = kc^n$‡, where $(dc/dt)_f > -(dc/dt)_r$, the concentration c will increase continuously, at the same time accelerating the consumption of reactant, so that at some instance the accumulation of the reactant will lead to the equation $(dc/dt)_f = -(dc/dt)_r$, which corresponds to a steady-state concentration c_{st} (at a given rate of supply this instant will occur sooner the greater is k)§. For a given feed rate this concentration is constant. If supply is slowed down, which corresponds to the condition $(dc/dt)_f < -(dc/dt)_r$, more of the substance will be consumed than is supplied, and a new stationary concentration $c'_{st} < c_{st}$ results.

In the case of the reactions under consideration here, taking place under conditions of high dilution, the stationary concentration determines the preferred direction of the process (formation of either a macrocyclic compound or a high polymer)[23]. The stationary concentration of the cyclisable substance depends not only on the rate of addition of the latter and the volume of the solvent but also, what is especially important, on the rate constant of the reaction. Different ring-closure reactions therefore require substantially different conditions of dilution, or give different results under the same conditions of dilution.

Let us examine by way of illustration two reactions obeying the same kinetic equation but differing in their rate constants (in particular, they may be represented by the same reaction in the presence of two different catalysts). In this case the stationary concentration c_{st} will obey the equation

$$\left(\frac{dc}{dt}\right)_f = -\left(\frac{dc}{dt}\right)_r = kc_{st}^n$$

whence

$$c_{st}^n = \frac{1}{k}\left(\frac{dc}{dt}\right)_f.$$

† In several cases, when the solubility of the cyclisable substance in the solvent used is negligible and the reaction is carried out in a heterogeneous medium, macrocyclic compounds can be obtained in a small volume of solvent without application of the high dilution technique (*e.g.* Ref. 47).

‡ The reaction velocity may depend not only on the concentration of the cyclisable substance but also on that of the condensing agent. However, the latter can be regarded as constant, so that all the arguments remain valid.

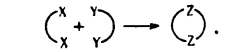
§ Strictly speaking, a stationary concentration is established if the duration of the reaction is infinite. If, for example, the substance is fed at a constant rate w, while it is consumed according to a first-order equation, the increase in concentration in the solution in unit time is $dc/dt = w - k_1c$. Integrating this expression, we obtain $t = -(1/k_1)\ln(1 - k_1c/w)$ or $k_1c/w = 1 - \exp(-k_1t)$. The condition of stationariness $k_1c/w = 1$ corresponds to $t = \infty$. In practice, however, the quantity $\exp(-k_1t)$ will become relatively small after a time determined solely by the rate constant. Thus if $k_1 = 0.1\ h^{-1}$ we have $k_1c/w \simeq 0.63$ after 10 h; if $k_1 = 1\ h^{-1}$ this ratio exceeds 0.99 even after 5 h; and when $k_1 = 10\ h^{-1}$ this state is reached after only 30 min.

If for two reactions (a and b) we choose the same rate of feed $(dc/dt)_{f,a} = (dc/dt)_{f,b}$, where $k_a > k_b$, we have $c_{st,a} < c_{st,b}$: *i.e.* the more rapid reaction corresponds to a lower stationary concentration, and so conditions will be more favourable for formation of the macrocyclic compound (*cf.* Ref. 48).

These relations apply also to the same reaction at different temperatures. Increase in the reaction rate constant with rise in temperature should result in a decrease in the steady-state concentration, just as should the use of a more active condensing agent. The upper temperature limit at which a given reaction can be carried out will, of course, depend on the thermal instability of starting materials or reaction products. In the high dilution technique variation in temperature depends on the choice of a solvent which is inert under the reactions conditions and boils at the required temperature. It must be noted that interaction of the solvent with the cyclisable substance may substantially affect the process of cyclisation by favouring either the "coiled" or the "open" form of the chain[23].

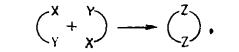
When reactions which occur at high dilutions are under discussion, it quite often becomes necessary to compare degrees of dilution. For this purpose we can use the relation[23] m/Vt, where m is the quantity of cyclisable substance, V the volume of solvent, and t the time during which the cyclisable substance is supplied. This ratio represents the quantity of cyclisable substance fed to unit reaction volume in unit time¶.

One variety of cyclisation is the synthesis of macrocyclic systems from two or more parts according to the scheme



Such a reaction undoubtedly takes place in two stages, with intermediate formation of a bifunctional compound of the type X–Z–Y.

Formation of a macrocycle from two segments is more difficult than direct cyclisation, since the high dilution required for the second stage of the reaction hinders occurrence of the first stage[23]. Therefore the synthesis of macrocycles from more than one segment yields good results only in especially favourable cases, for example if rigid groups are present in the initial compounds. This applies also to dimerisation of a bifunctional compound according to the scheme



which quite often accompanies normal cyclisation.

Actual methods of cyclisation are extremely varied, and can lead to macrocyclic compounds of various types (carbocyclic and heterocyclic, containing multiple bonds or aromatic rings, with various substituents). For brevity we shall merely mention the methods covered by Ziegler's review[23], and discuss in greater detail new work, selecting that concerned with a new reaction employed for cyclisation, and disregarding the routine application of an existing method.

¶ It is readily seen that $m/Vt = (dc/dt)_f$, and hence, if it is assumed that cyclisation is a first-order reaction, while the competing intermolecular reaction (polymerisation or polycondensation) is of the second order, it follows that

$$\frac{m}{Vt} = k_1 c_{st} + k_2 c_{st}^2.$$

If c_{st} is sufficiently small for the term $k_2 c_{st}^2$ to be neglected, we obtain $m/Vt \simeq k_1 c_{st}$.

Condensation of Dinitriles

The first preparative method of cyclisation employed for the synthesis of macrocyclic compounds was the condensation of dinitriles in the presence of sodium methylaniline using Ziegler's high dilution technique[31]. This method has been used to synthesise keto-nitriles containing rings of different sizes; the data obtained on the dependence of yield on ring size[49,50] have been repeatedly discussed in the literature and compared with yields obtained by other methods (see in particular Refs. 23, 34, and 46).

Cyclisation of Esters by the Dieckmann Reaction

The chemistry of this method is similar to that of the cyclisation of dinitriles, but this reaction has not been widely used in the formation of macrocycles because of the low yields obtained. It can serve for preparative purposes only if potassium t-butoxide or sodium hydride is employed as condensing agent and if the reaction is carried out in boiling xylene, the alcohol evolved in the reaction being distilled off. This procedure has been employed to obtain both carbocyclic and heterocyclic compounds. A more detailed account will be found in Ref. 51.

Cyclisation of Dicarboxylic Esters by the Acyloin Type of Condensation

This method has found the widest application for the synthesis of macrocyclic compounds. The reaction is carried out in boiling xylene over finely divided metallic sodium under the conditions suggested by Hansley[52] and worked out in detail by Prelog[53], Stoll[54], and their coworkers. It has already been mentioned above that chemisorption of an ester on the surface of molten sodium favours cyclisation. An important feature of the acyloin condensation is the very high reaction velocity under the given conditions, resulting in a low steady-state concentration of the diester. Because of this the yields of cyclic acyloins are quite high even without use of the high dilution technique. It is important to note that the acyloin condensation does not show such a sharp fall in yields in the range of medium rings as is characteristic of other methods. A disadvantage of the acyloin condensation is a certain experimental complexity: reaction must be carried out in the almost complete absence of oxygen with the use of a high-speed stirrer (rate of rotation of the order of 10 000 rev/min). Some modifications of the conditions of this condensation will be examined at the end of the present paper in connection with the problem of the synthesis of bicyclic systems containing a thiophen ring. It is noteworthy that in the seventeen years since publication of the work of Prelog and Stoll the method of carrying out the acyloin condensation has undergone no substantial change. Hence there is no need to discuss this reaction further.

Cyclisation by Intramolecular Alkylation

In several cases good results are obtained by this method. The cyclisation of ω-halogenoacylacetic esters to carbocyclic β-keto-esters developed by Hunsdiecker[55]

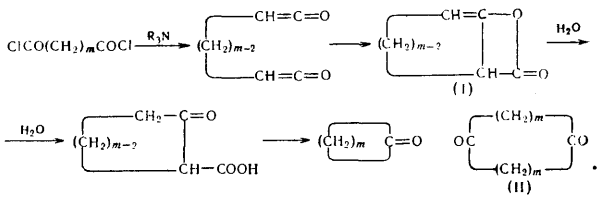
is well known. Several new applications of this reaction will be considered at the end of the paper.

Cyclisation of salts of long-chain ω-halogenoalkanoic acids to macrocyclic lactones is carried out under similar conditions. Among the papers of this latter reaction we shall mention only a fairly recent publication[56] on the kinetics of lactonisation.

Below we shall consider several new methods of cyclisation as well as some of the earlier methods which have recently found wide application.

Dimerisation of Ketens

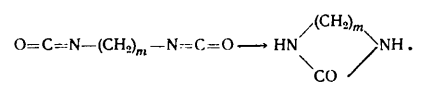
An interesting method of obtaining macrocyclic ketones was developed by Blomquist and his coworkers[57,58]. It is based on the dimerisation of ketens. Dichlorides of dibasic acids are converted by the action of tertiary amines into diketens, which under the conditions of high dilution undergo cyclisation to form analogues of the dimers (I). These "cyclic dimers of keten" are hydrolysed to β-keto-acids, which are readily decarboxylated, so that the reaction products are cyclic ketones. Formation of monoketones is accompanied by that of diketones of the type (II), products of the cyclisation of two molecules of the diketen.



Yields of this method are low (20–30%), but its simplicity enables it to be utilised for preparative purposes. In particular, civetone and (±)-muscone[58], as well as optical isomers of the latter[59], have been obtained in this way. An advantage of the method is the possibility of using relatively short-chain dicarboxylic acids, as can be seen in the synthesis of cyclohexadecanone[60]. Azelaoyl dichloride gives a 34% yield of cyclohexadecane-1,9-dione (II, $m = 7$), which is converted into a monothioacetal, this giving a 47% yield of cyclohexadecanone (based on the diketone) under the influence of Raney nickel.

Reduction of diketones over platinum gives hydroxy-ketones, from which cyclic homologues of civetone are formed by dehydration[61].

An analogous method in the heterocyclic series is the cyclisation of diisocyanates to cyclic ureas[62–65]:



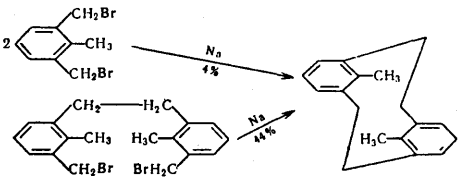
The latter method is probably similar in its chemistry to the cyclisation of azides of amino-acids under the conditions of the Curtius rearrangement, used for the preparation of unsymmetrical cyclic ureas[66].

Intramolecular Acylation

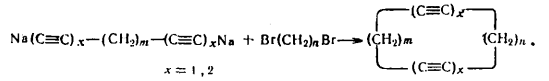
Intramolecular acylation by the Friedel–Crafts reaction has recently been widely developed, and has been investigated mainly by Huisgen and his coworkers on ω-phenylalkanoyl[48,67,68], ω-*p*-tolylalkanoyl[69], ω-1-naphthylalkanoyl[70], and ω-2-naphthylalkanoyl[71] chlorides as examples. We shall consider this method in greater detail at the end of the present paper, and note merely that cyclisation leads to products of different structures depending on the length of the aliphatic chain. For example, with ω-phenylalkanoyl chlorides $C_6H_5(CH_2)_mCOCl$ up to $m = 7$ cyclisation takes place in the *ortho*-position, but when $m \geq 8$ it occurs in the *para*-position.

Wurtz Reaction

Another classical process, the Wurtz reaction, also finds limited application in the synthesis of macrocyclic compounds. An interesting variant of the method is replacement of metallic sodium by its addition products with arylethylenes and aryl-dienes, in particular disodium tetraphenylethylene[72]. When the Wirtz reaction is used, the macrocycle is quite often built up from two segments. In this connection, a recent paper shows that such intermolecular cyclisation gives poorer results than intramolecular cyclisation[73]. In the synthesis of 4,12-dimethyl-[2,2]metacyclophane, yields at the cyclisation stage amount to 4% and 44% by the first and second methods respectively:



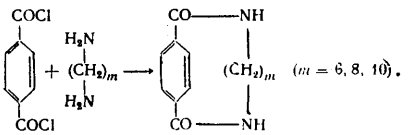
A similar mechanism to the Wurtz reaction is shown by the preparation of cyclic di- and poly-acetylenes from αω-dibromoalkanes and disodium derivatives of αω-diynes (see for example, Ref. 36):



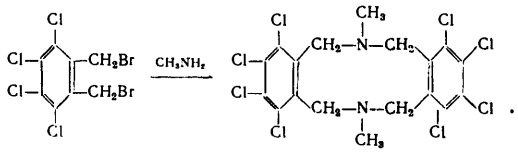
The paper referred to reports an interesting case of a "negative oxygen effect", the yield of the macrocyclic compound decreasing on introduction of oxygen into the chain. This phenomenon is explained[36] by an increase in the mobility of the cyclisable chain, resulting in an increase in the total number of possible conformations and thereby diminishing the effect of the rigid acetylenic groups.

Syntheses of Many-Membered Heterocycles Containing Aromatic Rings from Two or More Units

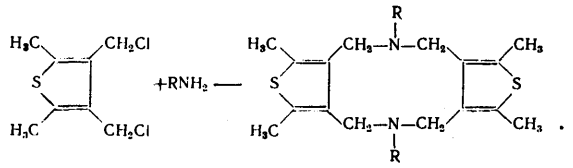
Several examples have been reported in which macrocycles are built in good yields from two or more units. We may note here the syntheses by Stetter and his coworkers of many-membered systems containing nitrogen and sulphur[74,75], for example



An interesting synthesis is that of the ten-membered dibenzodiazecine system, in more than 50% yield without use of the high dilution technique[76]



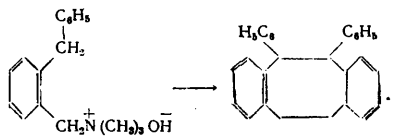
It is significant that under the same conditions the unsubstituted *o*-bisbromomethylbenzene gives high yields of *N*-methylisoindoline. Gol'dfarb and Kondakova have shown[77] that a ten-membered ring is readily formed also by reaction of 3,4-bischloromethyl-2,5-dimethylthiophen with primary amines:



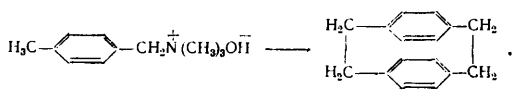
Such ease of formation of a ten-membered ring is unexpected. Gol'dfarb and Kondakova show[77] that this phenomenon is associated with the difficulty of cyclising a five-membered ring on to a thiophen ring, which is explained by the larger external angles associated with thiophen than with benzene (the $HC_{(3)}C_{(4)}$ angle is about 124° compared with 120°). It is possible that a somewhat similar phenomenon occurs in the case of tetrachloro-*o*-bisbromomethylbenzene. Polyhalogenobenzene molecules are known to be non-coplanar because of mutual repulsion between the halogen atoms, neighbouring halogen atoms being located on different sides of the ring (see, for example, data for hexachlorobenzene[78]). It is reasonable to assume that such non-coplanarity would hinder formation of a five-membered ring in comparison with the unsubstituted *o*-bisbromomethylbenzene. It may be added that in both cases cyclisation is favoured by the presence of rigid groups, and furthermore the diazecine system condensed with two benzene or thiophen rings may be considerably less strained than, for example, cyclodecane. However, the latter hypothesis requires experimental confirmation.

Syntheses *via* Quaternary Ammonium Bases

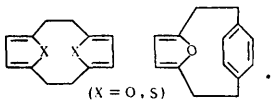
A very interesting method of preparing macrocyclic compounds containing aromatic rings which has recently been developed resembles chemically the Hofmann cleavage of quaternary ammonium bases. In the case of *o*-aralkylbenzylammonium hydroxide the Hofmann reaction yields substituted dibenzocyclooctadienes[79-82] for example



p-Aralkyl- or *p*-alkyl-benzylammonium hydroxides give the corresponding [2,2]paracyclophanes[83-85], for example



Similar methods have produced furan[84,85] and thiophen[84] analogues of [2,2]paracyclophane of the types

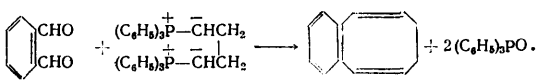


The mechanism of this cyclisation is not altogether clear. It is probable that intermediate compounds of *o*- or *p*-xylylene type are formed[84-87]. It is quite possible, however, that the reaction mechanism involves formation of an intermediate cyclic complex, as is indicated by the fact that substituents in the resulting macrocycle are always attached to adjacent carbon atoms, while structural isomers are not detected (see for example Refs. 81 and 83).

The comparatively high yields of the products obtained by this method (on the average about 30%), without requiring high dilution, are probably explained by the effect of the rigid groups.

Cyclisation by Means of the Wittig Reaction

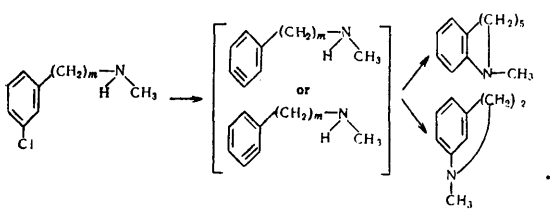
The Wittig reaction has also been used for the synthesis of macrocyclic compounds, although this method has not yet found wide application for this purpose. In 1958 Wittig and his coworkers described[88] the preparation of benzocyclooctatriene by the interaction of phthalaldehyde and the ylide formed from 1,4-dibromobutane and triphenylphosphine:



A synthesis of tetrabenzocyclohexadecaoctaene has been reported[89] in which the Wittig reaction has been used both to extend the chain and to close the macrocycle. Yields by this method are around 20–35%.

Cyclisation *via* Arynes

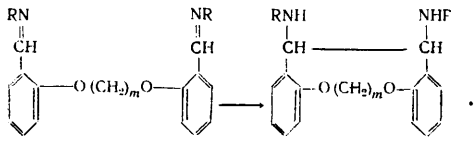
Among new methods must also be mentioned the synthesis of many-membered heterocycles containing a benzene ring by Huisgen and his collaborators[90,91]. This method uses the dehydrobenzene reaction and consists in the interaction under conditions of high dilution of a *m*-chloro-*N*-methylaminoalkylbenzene with sodamide or phenyllithium. Two examples of the reaction have so far been examined, and these show that cyclisation occurs in the *ortho*-, *meta*-, or *para*-position depending on the length of the aliphatic chain.



In the second case the *para*-cyclisation product is obtained as impurity (about 10% of the total quantity). Yields by this method are around 60%.

Cyclisation of Bisazomethines

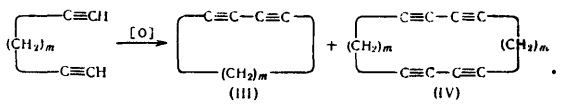
Another new method of synthesising macrocycles is the cyclisation of dianils by the action of finely divided metallic sodium[92] in ether or of aluminium amalgam[93] in a mixture of benzene and alcohol under conditions of high dilution. The reaction is essentially



Yields by the first method do not exceed 16%, and by the second fluctuate depending on m and R, reaching 40–60% with m = 3–9 and R = t-C_4H_9.

Oxidative Condensation of Diacetylenes

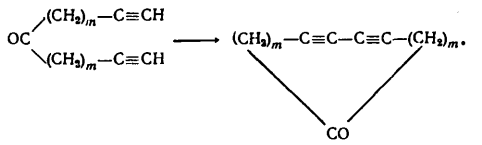
During the past six to eight years great progress has been made by the application of a new method of cyclisation based on the oxidative condensation of monosubstituted acetylenes. The long known method of condensing acetylenes in the presence of copper salts when applied to alka-$\alpha\omega$-diynes provides a route for the preparation of macrocyclic diacetylenes. In 1956 Eglinton and Galbraith[94] obtained from tetradeca-1,13-diyne under conditions of high dilution cyclotetradeca-1,3-diyne (III, m = 10) in yields up to 40%, with simultaneous formation of about 10% of the dimer (IV, m = 10):



Oxidation was effected with copper(II) acetate in a mixture of methanol and pyridine. Carrying out the reaction at smaller dilutions decreases the yield of the "monomer", while that of the "dimer" increases.

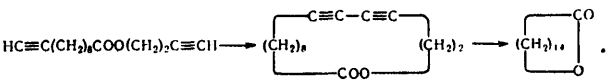
Almost simultaneously Sondheimer and his coworkers[95,96] obtained intermolecular cyclisations products of the type (IV) from the lower alkadiynes CH⋮C.$(CH_2)_m$.C⋮CH with m = 3–5. Oxidation was effected with air in aqueous alcohol at 55° in the presence of copper(I) chloride and ammonium chloride without use of the high dilution technique. Yields were low (2–12%) under these conditions, but subsequently, by using copper acetate in pyridine, Sondheimer *et al.*[97] obtained, together with "dimers", the "trimers", "tetramers", and in some cases "pentamers" in total yields of up to 40%. These products are easily separated by chromatography. From a purely preparative point of view, of course, this work of Sondheimer and his collaborators may be of no special interest, but it opens up a path to the preparation of many-membered conjugated cyclic polyenes, several of which, in conformity with Hückel's rule, should be aromatic in character[98–105].

The oxidative condensation of diacetylenes can be used not only to obtain hydrocarbons but also to synthesise functional derivatives, as well as heterocyclic compounds. Recently Bergel'son *et al.*[106] have described the preparation of cyclic diacetylenic ketones by the general reaction



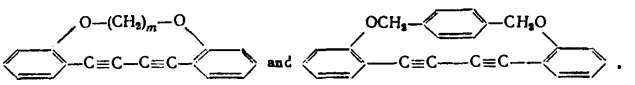
When the high dilution technique is used the yield is about 60% with values of 6 and 8 for m. The resulting ketones on hydrogenation give cycloalkanones, and in particular dihydrocivetone is obtained when m = 6.

This method has been used repeatedly to obtain cyclic esters[94,107–112], including those of dicarboxylic acids and glycols[94,107,112], as well as higher lactones[108–111]. When the high dilution technique is used (with a mixture of pyridine and ether as solvent), the yield on cyclisation reaches 80%,[109] so that oxidative condensation followed by hydrogenation has been suggested as a method for synthesising exaltolide[108]:



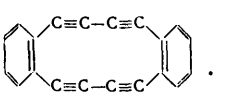
It is interesting that acetylenic macrocyclic lactones possess antibiotic activity[113].

Oxidative condensation has been used for the synthesis of ethers[114,115] of the types

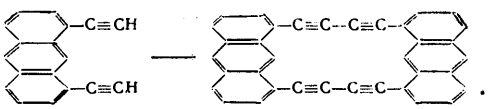


It has also been shown that cyclisation is in principle possible in the oxidative condensation of peptides containing ethynyl groups[116].

The fact that an acetylenic grouping is a "rigid group" plays an important part in the cyclisation of acetylenic compounds[107]. The effect of rigid groups is still greater when the molecule contains aromatic rings. For example, oxidative condensation of *o*-diethynylbenzene under conditions of high dilution gives a 43% yield of the highly strained cyclic molecule[117]†



The value of molecular rigidity is very clearly seen in the cyclisation of 1,8-diethynylanthracene[119]



† A similar type of product is formed also from 9,10-diethynylphenanthrene[118]. It is suggested in this paper[118] that formation of such strained molecules is made possible by an intermediate copper complex containing *o*-diethynyl compounds as ligands (a more detailed discussion of the significance of complex formation in the synthesis of macrocycles will be found in Section 4B).

A yield of 95% is obtained without the use of high dilutions. This result is not unexpected, since the rigidity of the initial molecule, with the ethynyl groups arranged in parallel, greatly diminishes the possibility of polycondensation. In other words, the conditions obtaining here correspond to Stetter's principle[44,45] already considered, according to which synthesis of a macrocyclic compound is facilitated if steric hindrance interferes with formation of a linear polycondensation product‡.

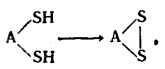
The mechanism of the synthesis of cyclic acetylenes by oxidative condensation has not been studied specially, but it is assumed[107] to be analogous to that established by Klebanskii *et al.*[121] for the polymerisation of linear acetylenes. This mechanism comprises a slow stage of acid dissociation and two rapid stages involving oxidation of the anion to a radical and dimerisation of the radicals:

$$RC{\equiv}CH \rightleftarrows RC{\equiv}C^- + H^+,$$
$$RC{\equiv}C^- + Cu^{2+} \rightarrow RC{\equiv}C^{\cdot} + Cu^+,$$
$$2RC{\equiv}C^{\cdot} \rightarrow RC{\equiv}C{-}C{\equiv}CR.$$

The univalent copper formed in the process is oxidised by air to bivalent copper, so that the process can occur with catalytic quantities of copper salts. In the case of $\alpha\omega$-diynes the resulting biradical $^{\cdot}C{\equiv}C{-}A{-}C{\equiv}C^{\cdot}$ can be stabilised either intramolecularly or intermolecularly with formation of various cyclic and linear products.

Cyclisation of Dithiols

The synthesis of cyclic disulphides by the oxidation of dithiols



has recently found important uses. Its application to alkane-$\alpha\omega$-dithiols has been studied systematically by Schöberl and Grafie[122]. This method is used in the synthesis of oxytocin and its analogues: first the polypeptide chain is built up, and then cyclisation is carried out, in the course of which the mercapto-groups of two cysteine groupings present in the chain are oxidised with formation of a disulphide bridge (see for example Ref. 12).

We shall not consider in detail the synthesis of porphyrins, since this question has been very fully discussed by Woodward[13], but we will examine isolated examples below. Here it may be pointed out merely that in these syntheses, as in those of azaporphins and phthalocyanines, the effect of rigid groups is of great significance[23], for as a result comparatively high yields of these extremely complicated compounds are obtained without the use of high dilutions. In this connection we may also note the synthesis of furan analogues of porphyrins[123].

Research on the synthesis of macrocyclic peptides and depsipeptides has developed considerably during recent years, in connection with proofs of the structure of several antibiotics, in particular gramicidin S and enniatins. This work lies far beyond the scope of the present review, and has been surveyed in some detail by Shemyakin in a monograph[9] and in a review paper[124]. Here it is relevant to note merely that the cyclisation stage in such syntheses consists in the formation of an amide link under conditions of high dilution, the usual methods of peptide synthesis being used to carry out this reaction, in particular the oldest and simplest of them, interaction of an acid chloride with a peptide having a free amino-group[125].

‡ At first sight this is contradicted by the observation that 1,8-bisbutadiynylanthracene forms the oxidative condensation product in only 17% yield[120]. However, the low yield of the macrocycle in this case is explained by the relative instability of the initial compound.

3. DEPOLYMERISATION

Degradation processes in macromolecular compounds with formation of macrocycles may be either reversible or irreversible, the first type being characteristic of heterocyclic compounds containing labile bonds, and the second of alicyclic compounds.

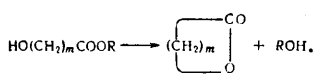
Reversible Processes

If polymerisation or polycondensation is reversible, we have in general the ternary equilibrium

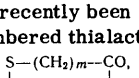
$$\text{polymer} \rightleftarrows \text{linear monomer} \rightleftarrows \text{cyclic monomer}.$$

An example of this type of process is provided by the polymerisation of ϵ-caprolactam, in which the lactam may be in equilibrium with 6-aminohexanoic acid and the polyamide. In the case of a many-membered cyclic monomer (eight-membered ring and larger) the above ternary equilibrium is almost entirely displaced towards the polymer[3]. If, however, the cyclic monomer is continuously removed from the equilibrium mixture, it can be obtained as the sole product. It was in this way that Carothers and his collaborators obtained monomeric and dimeric cyclic anhydrides of higher dicarboxylic acids[126], cyclic esters of glycols and dicarboxylic acids[127,128], and higher lactones[129]. Eight-membered salicylides and similar compounds have been obtained in an analogous manner[130,131]. Depolymerisation occurs on heating in a vacuum the corresponding polymeric anhydrides and polyesters in the presence of substances capable of cleaving the C–O bond (stannous chloride, magnesium chloride, magnesium oxide, etc.), provided that the macrocyclic compound is continuously removed. The patent literature indicates that the metals magnesium[132] and aluminium[133] are the most effective catalysts for the production of oxalactones and cyclic esters of dicarboxylic acids with glycols.

Subsequently Carothers' method of preparing lactones was improved. The process is considerably accelerated if depolymerisation is carried out in glycerol in the presence of a transesterification catalyst (an alkoxide[134,135] or an alkali-metal carboxylate[136]), the lactone distilling off in the glycerol vapour. Collaud[134], who first prepared an ester from glycerol monochlorohydrin and a sodium ω-hydroxyalkanoate, supposed that formation of a macrocyclic lactone involves an intramolecular transesterification§



§ Collaud's method has recently been employed[137] to obtain fifteen- and seventeen-membered thialactones of the type

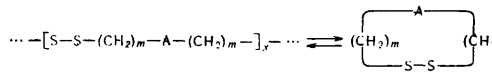


which, like many-membered ketones and lactones, possess a musk odour and strong fixative properties.

Such a change can undoubtedly occur under the reaction conditions, but is also clear that a polyester will then certainly be formed in the mixture: *i.e.* the mechanism of the process should by no means differ substantially from the depolymerisation of polyesters under the conditions suggested by Carothers[23]. The correctness of this view is confirmed by Belov *et al.*[136], who showed that there is no necessity to prepare an ester of the type $HO(CH_2)_mCOOR$ from a hydroxy-acid and glycerol: the previously prepared polyester can be subjected to depolymerisation in glycerol, when the yields exceed 80%, as in Collaud's method.

Higher lactones possessing a musk odour are of considerable interest for the perfumery industry. In this connection simple and practicable processes for obtaining the initial ω-hydroxyalkanoic acids are of great importance. At the present time it is very probably most reasonable to obtain ω-hydroxy-acids and lactones from them on the basis of ααωω-tetrachloroalkanes, which are products of the telomerisation of ethylene with carbon tetrachloride[138].

Not long ago a reversible process was described for the depolymerisation of polymeric disulphides[139,140]



This process takes place when the cyclic disulphide is removed together with water vapour; it is accelerated by addition of alkali.

It is interesting that thermal depolymerisation in a vacuum has been used even to obtain macrocyclic chelate compounds of beryllium from the corresponding chelate polymers[141]. Similar changes have recently been effected also by Korshak *et al.*[142], but, what is extremely significant, in dilute solutions instead of a vacuum. The possibility of shifting the equilibrium between polymer and cyclic monomer in favour of the latter by lowering the concentration of the solution has been discussed in detail by Strepikheev[143], who has shown in particular that, with ε-caprolactan at concentrations below 40 g litre^{-1}, the equilibrium is almost completely displaced towards the seven-membered ring. As far as I am aware, the above paper[142] provides the first example of the formation of macrocycles under conditions of this kind.

Synthesis of Macrocyclic Ketones by Ruzicka's Method

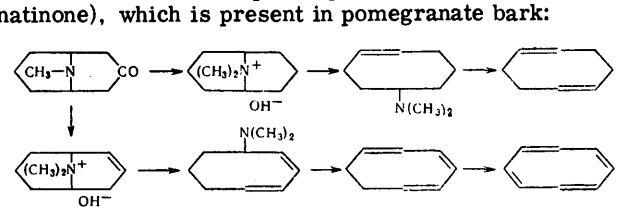
An example of an irreversible degradation process in which a macrocyclic compound is formed is Ruzicka's classical synthesis of macrocyclic ketones[29] by the pyrolysis of salts of higher dicarboxylic acids. In his opinion[144] the formation of cyclic ketones is due to the presence of small amounts of a cyclic form of the salts. However, Stoll and Rouvé showed[145]¶ that the results of pyrolysis do not depend on the method of preparation of the salt: even if during its precipitation the low concentration provided conditions favouring production of a cyclic form, the latter would be converted, owing to the reversibility of the double decomposition and hydrolysis, into the thermodynamically more stable linear form. Formation of a cyclic ketone occurs as a result of several segments of the chain coming together in the course of pyrolysis†, but the main product of pyrolysis is a polyketone. The opinion of Carothers and Hill[147] that in the pyrolysis of salts macrocyclic ketones are formed by reversible depolymerisation of polyketones, resembling what occurs with polyesters and polymeric anhydrides, cannot be regarded as sound. "Formation of cyclic ketones occurs not as a consequence of the depolymerisation of polyketones, as Carothers supposed, but in virtue of the 'depolymerisation' of salts of dicarboxylic acids at the instant of their conversion into ketones"[145].

4. SYNTHESES INVOLVING A TRANSANNULAR BOND

The first two groups of methods which we have considered — cyclisation and depolymerisation — are characterised by the fact that the many-membered ring is formed directly from a linear molecule. The characteristics of such a process make it necessary to carry out the reaction under conditions of dilution or with continuous removal of the macrocyclic compound from the equilibrium mixture, which, of course, to some extent limits the practical application of these methods. Restrictions of this type do not exist in syntheses involving a transannular bond, the essence of which is that the macrocycle is formed directly not from a linear molecule, but from a bicyclic or polycyclic system, in the construction of which only the comparatively readily formed three–seven-membered, predominantly five- and six-membered, rings are closed. Scission of the transannular bond, resulting in formation of the macrocycle, is quite often accompanied by the appearance of substituents at the point of cleavage, which enable further reactions to be carried out. A considerable number of syntheses of macrocyclic compounds based on this principle are now known. They can be classified into three groups — (A) scission of one or more bonds in a bi- or poly-cyclic compound, (B) synthesis of a macrocycle with intermediate formation of coordinate bonds, and (C) valency isomerisation.

A. Scission of One or More Bonds in Bicyclic and Polycyclic Compounds

Classical examples of reactions of this type are Willstätter's syntheses of cyclooctadiene[148-150] and cyclooctatetraene[151,152] from the alkaloid pseudopelletierine (*N*-methylgranatinone), which is present in pomegranate bark:

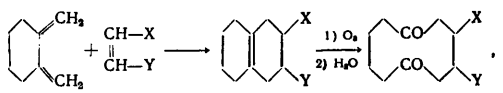


¶ Stoll and Rouvé's paper was published in 1944, but was not discussed in Ziegler's review[23], and therefore it is considered here in some detail. It is especially important because it demonstrates the untenability of the usual view of Ruzicka's method as a cyclisation reaction.

† Such approach may result in the intermediate formation of a cyclic salt, but in the light of modern views of the thermal decomposition of salts of carboxylic acids as passing through a cyclic active complex[146] such a stage must not be regarded as necessary for the production of a cyclic ketone.

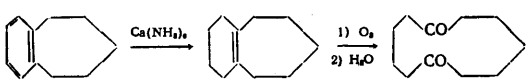
The unusual properties of the hydrocarbons obtained by Willstätter led to doubt being cast on these syntheses for some forty years. It was only in 1948 that Cope and Overberger[153] repeated the synthesis of cyclooctatetraene, and in 1950 Ziegler and Wilms[154] repeated that of cycloocta-1,5-diene, and showed that Willstätter and his collaborators had actually been the first to obtain these compounds. Both the American and the German workers used synthetic pseudopelletierine instead of the natural product for the synthesis, obtaining it in about 50% yield by the Robinson–Schöpf method from glutaraldehyde, methylamine, and acetonedicarboxylic acid. Phenylcyclooctatriene was also obtained from pseudopelletierine[155].

Macrocyclic compounds can be obtained from fused as well as from bridged systems. Thus the synthesis of cyclodecane-1,6-dione by the ozonisation of Δ^9-octahydronaphthalene followed by hydrolysis of the ozonide, proposed by Hückel *et al.*[156], has been used many times by other investigators to obtain cyclodecane derivatives[157,158]. In 1957 Bailey and Golden[159] prepared a series of substituted Δ^9-octahydronaphthalenes by diene synthesis from 1,2-dimethylenecyclohexane, and converted them by ozonolysis into the corresponding cyclodecane derivatives:



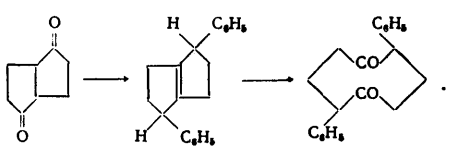
where X = H while Y = NO_2, $NHCOCH_3$, $NHCOC_6H_5$, COOH, and X = Y = COOH. The yields at the ozonolysis stage are 40–60%.

In a similar manner Plattner[160] obtained cycloundecane-1,6-dione from benzocycloheptene:

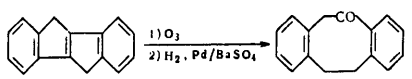


The sesquiterpene alcohol guaiol has been converted by dehydration followed by hydrogenation into 3-isopropyl-6,10-dimethylbicyclo[5,3,0]dec-1(5)-ene, from which the corresponding trialkylated cyclodeca-1,5-diene was obtained by ozonolysis[161].

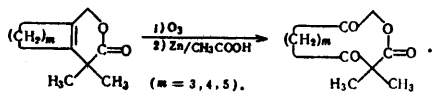
Ozonisation has also been used to obtain cyclooctane derivatives. Wawzonek[162] converted bicyclo[3,3,0]octane-2,6-dione into 2,6-diphenylcyclooctane-1,5-dione according to the scheme



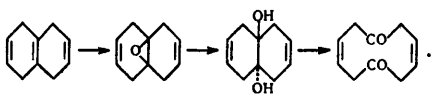
If the ozonide is not decomposed with water, but hydrogenated, a monoketone can be obtained, as has been shown in the case of dibenzocyclooctadienone[163]:



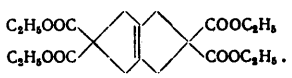
Ozonisation can be used to obtain not only carbocyclic but also heterocyclic compounds. A paper has recently appeared[164] on the synthesis of diketo-lactones of medium ring size by the series of reactions



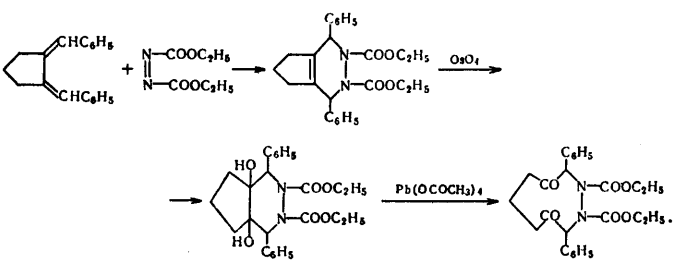
Methods of oxidation other than ozonisation can be used to cleave a C=C double bond, and this is essential if the initial compound contains more than one multiple bond. For example, Grob and Schiess[165] oxidised 1,4,5,8-tetrahydronaphthalene to the corresponding 9(10)-oxide with perbenzoic acid; the product was hydrolysed, and oxidation of the resulting glycol with lead tetraacetate in methanol gave cyclodeca-3,8-diene-1,6-dione:



A similar sequence of reactions has been used to convert indane into cyclonon-7-ene-1,5-dione[166]. Cope and Kagan[167] used performic acid or osmium tetroxide followed by lead tetraacetate to cleave the C=C bond in tetraethyl bicyclo-[3,3,0]oct-1(5)-ene-3,3,7,7-tetracarboxylate

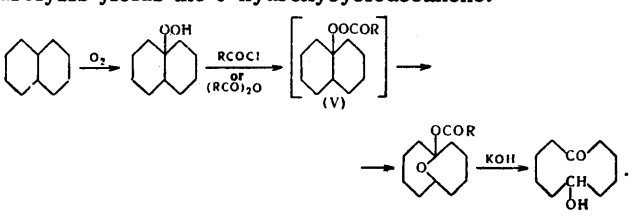


The method of oxidative cleavage of a double bond has also been used to obtain a many-membered heterocycle[168]:



Yields at the two stages of oxidative cleavage are around 60%.

An important reaction for converting decahydronaphthalene into 6-hydroxycyclodecanone was discovered by Griegee[169–172]. Oxidation of decalin with oxygen at 110° gives a hydroperoxide, which rearranges under the influence of an acid anhydride or chloride into an ester of 11-oxabicyclo[4,4,1]undecan-1-ol, and this on alkaline hydrolysis yields the 6-hydroxycyclodecanone:

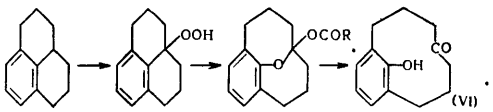


The reaction involves intermediate formation of an unstable hydroperoxide ester (V). The acetate and the benzoate of the hydroperoxide rearrange on being heated, the *p*-nitrobenzoate can be isolated only by working very rapidly, and

the trichloroacetate cannot be isolated at all[171]. In the last two cases the yields of the 11-oxabicyclo[4,4,1]undec-1-yl ester are 68% and 62% respectively based on the hydroperoxide[172]. In spite of the moderate yields of the hydroperoxide (~ 25%)[173], the ready availability of the starting material and the simplicity of the operations make this method of great interest, and it can be used for preparative purposes. A well-known simplification of Criegee's method is to obtain 11-oxabicyclo[4,4,1]undec-1-yl acetate in one stage[173] by the action of oxygen on a mixture of decalin and acetic anhydride, but the yield of the ester is then only 15% based on the decalin which has reacted. Rearrangement of the hydroperoxide to 6-hydroxycyclodecanone can be effected simply by heating it in t-butyl alcohol in the presence of sulphuric acid[173], the yield being 25%.

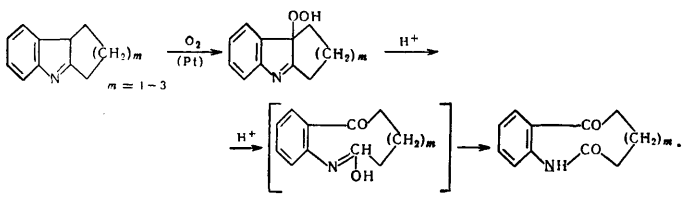
Hexahydroindane behaves similarly to decahydronaphthalene[174]: the hydroperoxide which it forms is converted by *p*-nitrobenzoyl chloride into the 10-oxabicyclo[4,3,1]-dec-1-yl ester (in 58% yield), hydrolysis of which gives a 74% yield of 5-hydroxycyclononanone.

The above process can also be applied to more complicated tri- and tetra-cyclic systems[175-177], for example hexahydrophenalene[175]

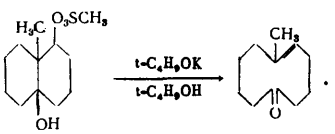


Bicyclic products of the type (VI) are not formed if the aliphatic chain linking the *meta*-position of the benzene ring contains less than seven carbon atoms[177,178].

The method of scission of a C–C bond via a hydroperoxide has been applied also to tetrahydrocarbazole and its cyclic homologues[179]:

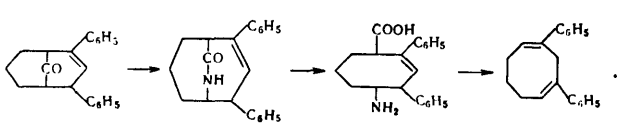


The bicyclic decahydronaphthalene system can be converted into a monocyclic system also by the so-called "fragmentation" reaction, effected by the action of potassium t-butoxide in t-butyl alcohol on methanesulphonic monoesters of 1,3-diols[180]

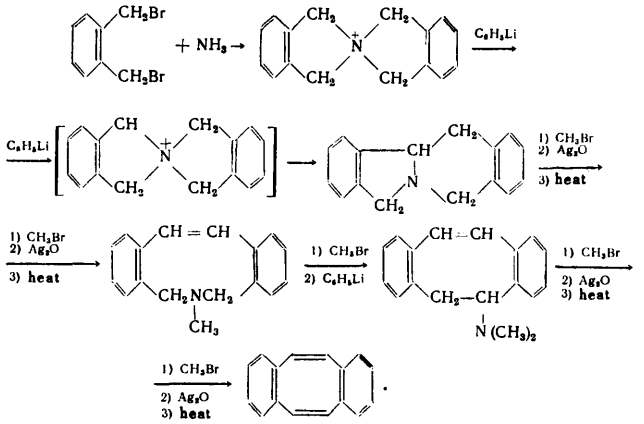


This reaction has found application for the conversion of fused six- and five-membered rings into a nine-membered ring in the synthesis of caryophyllene and isocaryophyllene[181].

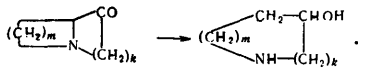
Rupture of the transannular bond can be accomplished in appropriate cases also by a reaction such as the Beckmann rearrangement[182,183]:



Wittig *et al.*[184,185] synthesised eight- and twelve-membered systems fused with benzene rings. The synthesis was based on successive application of the Stevens rearrangement and the Hofmann degradation, as can be seen from the scheme

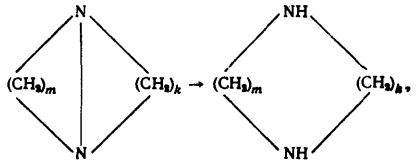


In several cases reductive cleavage of a C–N or an N–N bond is used in the synthesis of many-membered heterocycles. The work of Leonard and his coworkers[186-189] shows repeated applications of the electrochemical reduction of bi- and tri-cyclic amino-ketones, *e.g.* according to the scheme



The initial amino-ketones with $m = 3$, 4 and $k = 2-5$ were obtained by a Dieckmann condensation.

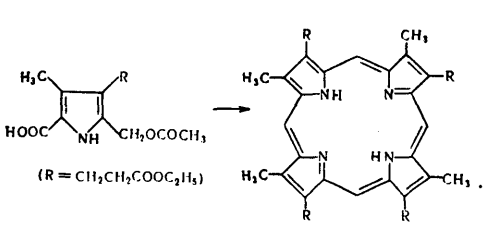
Stetter and Spangenberger[190] described several examples of the cleavage of an N–N bond in bicyclic hydrazines under the influence of Raney nickel:



where $m = k = 3$, $m = k = 4$, and $m = 3$, $k = 4$.

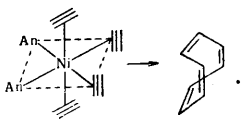
B. Syntheses with Intermediate Formation of Coordinate Bonds

Coordinate as well as covalent bonds can fill the role of the auxiliary transannular linkage. It has repeatedly been pointed out (see in particular Ref. 23) that, in the synthesis of porphyrins and phthalocyanines, the presence of metal salts may assist formation of a macrocycle in virtue of complex formation. For example, the synthesis of coproporphyrin III in conformity with the accompanying scheme[191] gives a yield of 29%

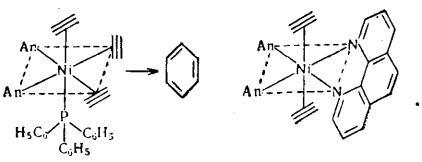


When this cyclisation is carried out in the presence of cobaltous chloride the yield increases to 52%, and, of course, a cobalt complex of the porphyrin is formed, the molecule of which consists of fused five- and six-membered rings. Its conversion into the metalfree porphyrin presents no difficulty. This type of synthesis of macrocyclic ligands, passing through a polycyclic chelate compound as intermediate stage, has been generalised in a recent review by Busch[192]. Below we shall discuss methods of practical importance for obtaining unsaturated hydrocarbons containing eight-, ten-, and twelve-membered rings, with the intermediate formation of coordinate links.

Coordination of four acetylene molecules around a nickel atom is observed in Reppe's synthesis of cyclooctatetraene[193]. Only compounds of bivalent nickel in which the cation is not very firmly bound to the ligands, so that the latter can be replaced by acetylene although it is a weak ligand, can act as catalysts in the Reppe synthesis. The catalysts used are nickel cyanide[193] and various chelate complexes of bivalent nickel (with acetylacetone[194], acetoacetic ester[194], salicylaldehyde[194], salicylaldimine[194,195], and *N*-alkylsalicylaldimines[195]). It is supposed[195] that in the transition state the ligands are arranged at the corners of an octahedron, with the nickel cation at its centre, two of the corners being occupied by anions, and the remaining four corners by acetylene molecules bound as a π complex



Formation of the π complex facilitates the passage of sp hybridisation (the acetylene molecule) into sp^2 hybridisation (cyclooctatetraene)[195]. Addition of organic bases, which are able to take the place of acetylene in the transition complex, lowers the yield of cyclooctatetraene[196]. In particular, the latter is not formed at all in the presence of triphenylphosphine[196]. It has been found[195] that under such conditions the acetylene undergoes trimerisation to benzene. This is explained[195] by the $P(C_6H_5)_3$ molecule occupying one corner of the octahedron, while acetylene is coordinated at the three corners remaining vacant. It is significant that in the presence of phenanthroline, which occupies two coordination positions, no reaction at all occurs between the acetylene molecules[195].



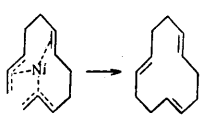
The view is also held[197] that cyclooctatetraene may be formed *via* a complex of cyclobutadiene with the nickel salt, which is unstable in the free state. Experimental data exist which indicate that the conversion of nickel complexes of cyclobutadiene[198] and tetramethylcyclobutadiene[199] into cyclooctatetraene and octamethylcyclooctatetraene respectively, is in principle possible. However, whether the synthesis of cyclooctatetraene does actually pass through a cyclobutadiene stage remains an open question, since the yield of cyclooctatetraene from acetylene is far higher, and reaction occurs under milder conditions, than in the case of synthesis *via* the cyclobutadiene complexes. It may be noted, incidentally, that the above two views are not mutually exclusive, since in the transition state depicted above two acetylene molecules are very conveniently arranged for the formation of cyclobutadiene, and if the latter is formed, it is automatically present as a nickel complex.

In any case, it can be seen from the above that the production of cyclooctatetraene from acetylene involves an auxiliary transannular bond. Substituted cyclooctatetraenes can be obtained similarly from the corresponding substituted acetylenes[200-202].

Besides bivalent nickel compounds, complexes of zerovalent nickel can also be used[202,203] as catalysts for the tetramerisation of acetylene. The Reppe synthesis of cyclooctatetraene gives a high yield (exceeding 70%)[194], and at the present time cyclooctatetraene is the main source for preparing eight-membered carbocyclic systems.

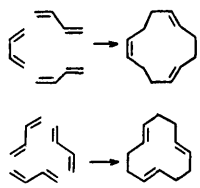
Another important method for obtaining eight-membered rings is the cyclodimerisation of butadiene to cycloocta-1,5-diene by means of zerovalent nickel stabilised as a complex of the type $(R_3P)_2Ni(CO)_2$ (where R represents phenyl[204], phenoxyl[204,205], or methoxyl)[204,205] or else as compounds of general formula $[(C_6H_5)_3X]_4Ni$ (where X = P, As, Sb)[206]. Isoprene[207,208] and penta-1,5-diene[207] can also undergo cyclodimerisation under these conditions.

Cyclodimerisation is accompanied to a greater or lesser extent by cyclotrimerisation, which becomes the main process when π complexes of zerovalent nickel with olefins are used[206,209], butadiene being converted in high yields into cyclododeca-1,5,9-triene. This reaction, like the tetramerisation of acetylene, involves formation of a π complex of butadiene with nickel. An intermediate π complex of nickel with a linear trimer of butadiene has been isolated[210], and then under the action of excess of butadiene or of another substance binding Ni^0 into a complex (for example carbon monoxide) converted into cyclododeca-*trans*-1,*trans*-5,*trans*-9-triene



A similar mechanism[211] is suggested for the synthesis of cyclododeca-1,5,9-triene in the presence of mixed organoaluminium catalysts, like that proposed by Ziegler for the polymerisation of olefins. The first stage in this synthesis is the formation of a π complex from three molecules of butadiene and a transition metal (chromium or titanium); in this complex three new C–C bonds are established, after which the cyclododecatriene is separated from the metal atom, which can then enter into a new cycle of reactions. Aluminium–titanium catalysts (mixtures of titanium tetrachloride or trichloride with alkylaluminium chlorides) or aluminium–chromium catalysts (mixtures of chromyl chloride with a trialkylaluminium or a dialkylaluminium hydride) are used for the trimerisation of butadiene. Its low-temperature (40°) trimerisation at normal pressure gives in the first case an approximate 90% yield of cyclododeca-*cis*-1,*trans*-5,*trans*-9-triene[212,213]. In the second case a total yield of 90% is obtained of a mixture

comprising 60% of the *trans-trans-trans*-triene and 40% of the *cis-trans-trans*-isomer[212,213]:

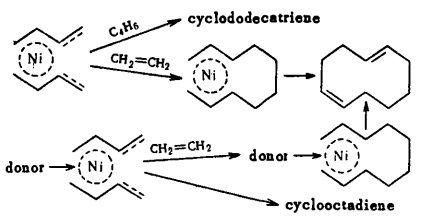


Other 1,3-dienes, in particular isoprene, penta-1,3-diene, and 2,4-dimethylpenta-1,3-diene, can also undergo cyclotrimerisation[213-215].

At the present time cyclodecatrienes are the principal starting materials for the preparation of various twelve-membered carbocyclic compounds and the reaction products. Especial interest attaches to the production from cyclododecatrienes of decane-1,10-dicarboxylic acid and ω-aminolauric acid and its lactam, which are starting materials for the synthesis of valuable polyamides[212,213]. Several papers and patents have been published on the production of these substances (*e.g.* Refs. 216–223).

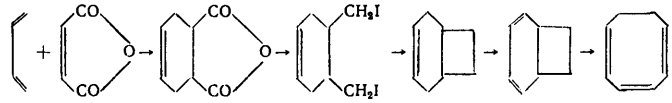
A recent paper[224] has described the preparation in high yields (up to 80%) of cyclodeca-*cis*-1,*trans*-5-diene from butadiene and ethylene by means of zerovalent nickel.

The formation of eight-, ten-, and twelve-membered cycloalkenes is assumed to have a similar mechanism[224]. Interaction of butadiene with nickel yields initially an unstable complex containing two molecules of butadiene per atom of the metal. The action of excess of butadiene on this complex produces cyclododecatriene (*via* a 3 : 1 butadiene–nickel complex). If, however, ethylene is present in the reaction mixture, it combines with the initial complex in preference to butadiene (perhaps steric factors are operative here) and forms cyclodecadiene. When stable complexes of Ni^0 with electron-donors (*e.g.* phosphorus compounds) are employed as catalysts, the 3 : 1 complex cannot in general be formed, and cycloocta-1,5-diene is obtained in yields up to 95%; in the presence of ethylene the formation of cyclooctadiene may be accompanied by that of cyclodecadiene (for greater detail see Ref. 224; *cf.* also with the above mechanism for the cyclotetramerisation of acetylene).



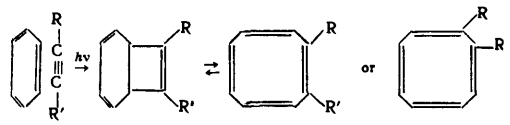
C. Valency Isomerisation of Cyclic Systems

In this section we shall consider several methods based on the isomerisation of compounds containing normal rings into macrocyclic compounds, where the equilibrium can be displaced to one side or the other depending on the size of the ring. This group now includes a fairly large number of examples of the preparation of unsaturated eight-membered systems from the corresponding mono- and bi-cyclic compounds by the so-called Cope rearrangement. The first work known to the Reviewer in which this method was intentionally used was carried out by Alder and Dortmann[225], who started from butadiene and maleic anhydride and synthesised cycloocta-1,3,5-triene via bicyclo[4,2,0]octa-2,4-diene:



The last stage in the synthesis was based on the work of Cope *et al.*[226], who found that a dynamic equilibrium is established between bicyclo[4,2,0]octa-2,4-diene and cycloocta-1,3,5-triene at 80–100°, with the monocyclic structure predominating (85%). This reaction forms the basis for the preparation of dimethyl cyclooctatrienedicarboxylate from diene synthesis products of cyclobutene-1,2-dicarboxylic ester with butadiene[227,228] and 1,4-dichlorobutadiene[228].

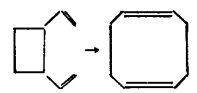
The well-known isomerism of cyclooctatetraene and bicyclo[4,2,0]octa-2,4,7-triene[193,229] is utilised in the preparation of substituted cyclooctatetraenes from photoadducts of benzene and the corresponding acetylenes[230,231]:



where R = R′ = $COOCH_3$, R = $COOCH_3$, R′ = H, R = C_6H_5, R′ = H, R = R′ = H.

1,2,3,4-Dibenzocyclooctatetraene can be obtained from the corresponding tetracyclic system[232].

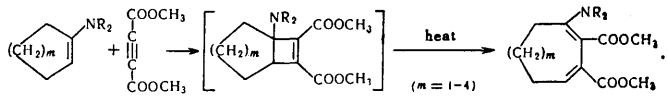
Monocyclic *cis*-1,2-divinyl-cyclobutane and -cyclopropane undergo similar changes, cycloocta-1,5-diene being formed in the first case[233,234]:



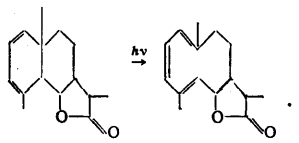
Vogel suggested[235] that the corresponding cycloocta-1,5-dienes, formed together with the normal products of diene synthesis in the thermal dimerisation of butadiene[154,236], chloroprene[237,238], and 2,3-dichlorobutadiene[238] (in the last case as the sole product of dimerisation), are obtained *via* divinylcyclobutane and its chlorinated derivatives. This hypothesis on the mechanism of dimerisation can probably be extended to isoprene and penta-1,3-diene, from the thermal dimerisation products of which Nazarov *et al.*[239,240] isolated the corresponding dimethylcyclooctadienes. In this connection it may be mentioned that 1,5- and 1,6-dimethylcycloocta-1,5-dienes have recently been found among the products of the thermal isomerisation of four-membered cyclic dimers of isoprene[241,242].

It is interesting that in the cases of 1,2-divinylcyclopentane[243] and 1,2-divinylcyclohexane[244] the equilibrium is displaced towards the products containing normal rings, so that an analogous method cannot be used to obtain compounds containing nine- and ten-membered rings.

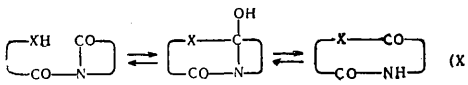
Valency isomerisation has been employed in the synthesis of substituted cycloalka-1,3-dienes via enamines[245]:



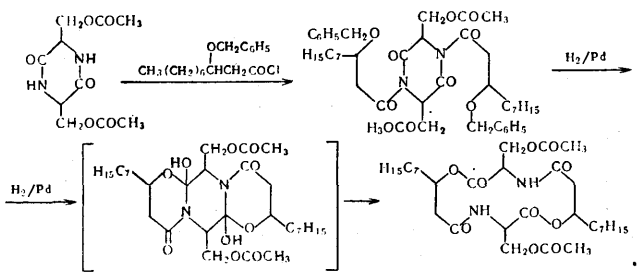
A recently published synthesis of dihydrocostunolide[246] includes as an intermediate step the photolytic conversion of the cyclohexa-1,3-diene into the hexatriene system:



In the opinion of the Reviewer the novel method of synthesising cyclic peptides and depsipeptides discovered by Shemyakin and his coworkers[247-249], which they term aminoacyl and hydroxyacyl insertion in peptide systems, can be included among valency isomerisation methods. It is based on the equilibrium between ω-aminoacyllactams (or ω-hydroxyacyllactams), cyclols, and cyclopeptides (cyclodepsipeptides):

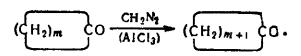


The position of equilibrium depends on the size of the ring[249]. In particular, cyclodepsipeptides are formed beginning with an eleven-membered ring; when ten-membered rings can be obtained, transannular interaction of CO and NH groups is appreciable; but nine-membered rings cannot be obtained at all, the stable form in these cases being the cyclol or an equilibrium mixture of the latter and the ω-hydroxyacyllactam. An important success of this method has been the synthesis of the antibiotic serratamolide. This synthesis is interesting also because it is evidently the first example of the preparation by means of a transannular bond fission of a compound containing a large ring (not a medium ring, as is usual):



5. RING ENLARGEMENT AND CONTRACTION

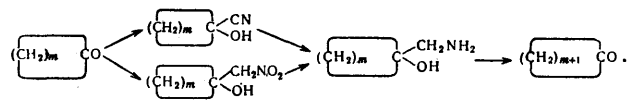
Processes of ring enlargement may yield either a higher cyclic homologue or a compound of a different type. Examples of the first class are the reactions of cyclic ketones with diazomethane, and of the second class the Dem'yanov isomerisation of rings and the Beckmann rearrangement of cyclic ketones. The reaction of cyclic ketones with diazomethane usually gives low yields and produces mixtures of cyclic homologues. Therefore it is little used for preparative purposes[23]. Recently, however, Müller and his collaborators[250-252] have found that in the presence of Friedel-Crafts catalysts the reaction gives high yields (up to 80%) and one product is mainly formed, a ketone containing one cyclic CH_2 group more than in the starting material:



This reaction has been verified by the synthesis of ketones from cycloheptanone to cyclopentadecanone. Diazoethane[252,253] and diazopropane[252] give respectively 2-methyl- and 2-ethyl-cycloalkanones, the yields being no lower, and in the case of diazoethane even higher, than with diazomethane.

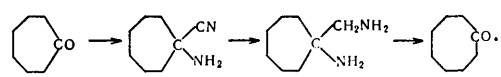
The Dem'yanov rearrangement has been used many times to obtain macrocyclic alcohols and ketones. As early as 1907 Wallach converted aminomethylcycloheptane into cyclooctanol[254]. In 1926 Ruzicka and Brugger[255] prepared cyclononanol in an analogous manner.

Deamination of 1-aminomethylcycloalkanols yields ketones[256]. Since amino-alcohols of the required type are readily obtained from ketones, this procedure enables us to pass from a lower to a higher ketone. This is accomplished by converting the ketone into a cyanohydrin, which gives the amino-alcohol on reduction with hydrogen over platinum oxide[257,258] or with lithium tetrahydroaluminate[216,259]. Another route for obtaining 1-aminomethylcycloalkanols consists in condensation of the ketone with nitromethane followed by electrolytic reduction of the nitromethylcycloalkanol[260]:

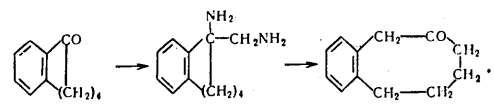


Cyclooctanone[259,261,262], cyclononanone[257,261,262], and cyclotridecanone[216] have been obtained by deamination of the corresponding amino-alcohols.

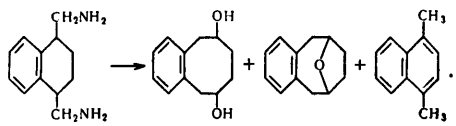
Ketones can be obtained also by the deamination of 1-amino-1-aminomethylcycloalkanes[263], which are readily synthesised from ketones, for example



This reaction has been employed also in the benzocycloalkenone series[264]:

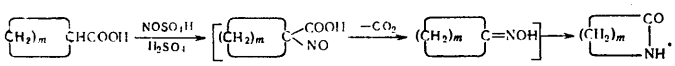


The Dem'yanov rearrangement occurs also with bisaminomethyltetrahydronaphthalene[265], but the reaction is complicated by side-reactions:



Several methods of ring enlargement are specific to the formation of heterocyclic compounds. Thus an important method which allows us to pass from alicyclic to heterocyclic compounds is the Beckmann rearrangement of cycloalkanone oximes[266,267]. This rearrangement has been employed also in the benzocycloalkanone[48,268] and thienocycloalkanone[269] series.

Recently a method has been developed for obtaining lactams by the action of nitrosyl sulphate on cycloalkanecarboxylic acids:

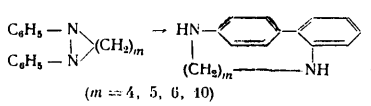


In particular, this method has been used to convert cyclooctanecarboxylic acid into octane-8-lactam[270], and cyclododecane- and cycloundecane-carboxylic acids into the ω-lactams of lauric and undecanoic acids respectively[271].

The Schmidt rearrangement is also utilised[272] to obtain macrocyclic lactams.

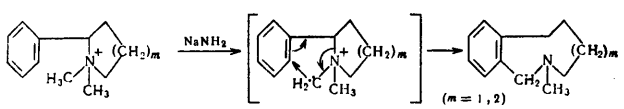
Cyclic ketones can be converted into many-membered lactones by oxidation with Caro's acid[273] or perbenzoic acid[274].

We may note also work on the benzidine rearrangement of *NN'*-polymethylenehydrazobenzenes[275,276]:

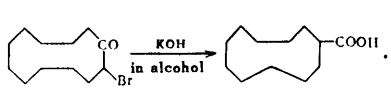


($m = 4, 5, 6, 10$)

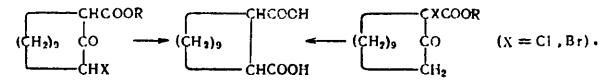
A many-membered heterocycle can be built up also by use of the Sommelet rearrangement[277,278]:



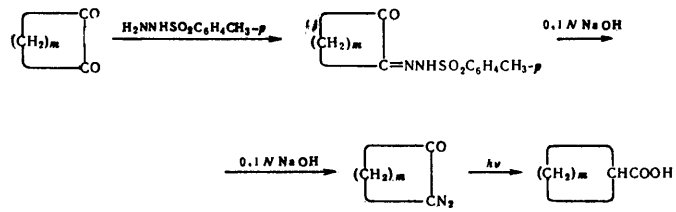
In some cases methods of ring contraction are of preparative interest. As already mentioned, compounds containing a twelve-membered ring have recently become available. In this connection work has been published[279,280] on the conversion of 2-bromocyclododecanone by a Favorsky rearrangement into cycloundecanecarboxylic acid:



Similarly, 1- and 3-halogeno-2-oxocyclododecanecarboxylic esters are converted into cycloundecane-1,2-dicarboxylic acid [formed as a mixture of the (±)- and *meso*-forms][281]:



We may also note ring contraction in cyclic diazo-ketones[282] (Wolff rearrangement). The diazo-ketones are obtained from 1,2-diketones, which are formed by the oxidation of acyloins. These changes are illustrated by the scheme



This reaction has also been utilised in the paracyclophane series[283].

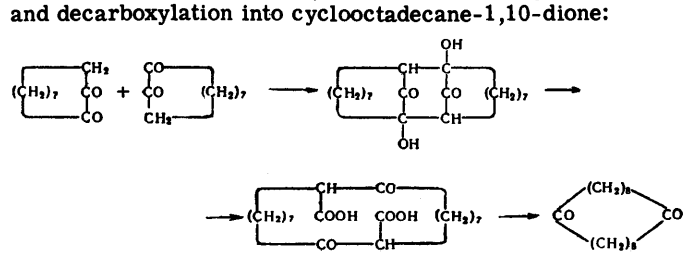
In some cases the conversion of many-membered cyclic bisazo-compounds into tetraphenylcycloalkanes, in which high yields are obtained, may prove useful[284,285].

6. COMBINED METHODS

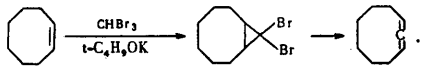
The present section examines methods which strictly belong to none of the above four groups. However, they can be regarded as a combination of two methods, for example the transannular bond method combined with cyclisation or ring enlargement. In all cases to be considered below, the synthesis passes through the stage of a bicyclic or polycyclic compound, but, in contrast to the transannular bond method, these intermediate compounds already contain the macrocycle as a structural unit, obtained either by cyclisation, by the transannular bond method, or by ring enlargement.

Thus Leonard *et al.*[187,188] found eight-membered rings among the bi- and tri-cyclic amino-ketones which they obtained by the Dieckmann reaction; on electrolytic reduction these compounds were converted into twelve-membered cyclic amino-alcohols.

Raphael and Scott[286] obtained a tricyclic compound by the self-condensation of cyclodecane-1,2-dione in the presence of sodium methoxide, and converted it by oxidation and decarboxylation into cyclooctadecane-1,10-dione:

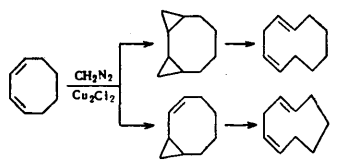


Higher cycloalkenes are converted by the action of dibromocarbene into bicyclic systems, which in the presence of methyllithium[287] or metallic magnesium[288] are transformed into cyclic allenes containing one carbon atom more than in the original cycloalkene, for example

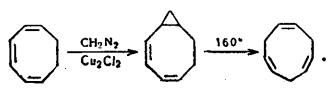


Cyclic dienes having isolated double bonds react at either one or two double bonds depending on the size of the ring[287]

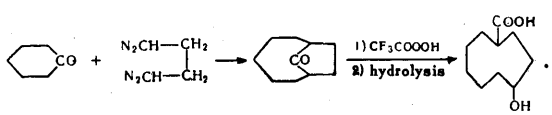
The action of diazomethane on cyclic dienes in the presence of copper(I) chloride gives the corresponding fused bi- and tri-cyclic systems, which at 310–345° rearrange into monocyclic dienes, for example[289]



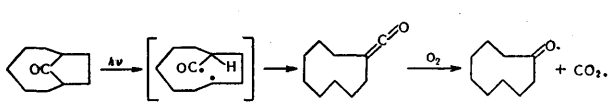
A similar reaction occurs with cyclic trienes[290]



A further method of synthesising compounds containing a medium ring, which is of theoretical interest, is based on a combination of ring enlargement with the transannular bond method[291,292]. Interaction of cyclohexanone and cyclopentanone with 1,4-bisdiazobutane produces bridge ketones, which are then converted into nine- and eight-membered monocyclic compounds, for example

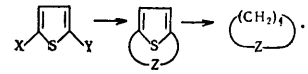


An extremely interesting way of converting a bridge ketone into a monocyclic ketone is photolysis followed by treatment with oxygen[293]:



Combined methods include also the novel synthesis of macrocyclic compounds developed by Gol'dfarb and his coworkers[294-307], which is based on the reductive desulphurisation of thiophen derivatives by the action of Raney nickel.

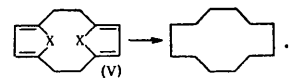
The method consists essentially in cyclisation of a long-chain bifunctional thiophen compound to form a bi- or poly-cyclic compound containing the thiophen ring, followed by elimination of sulphur with Raney nickel, resulting in the formation of an alicyclic compound‡:



An important feature of the present method is that thiophen is used not only to build up the skeleton by lengthening the chain by four carbon atoms but also as a "rigid group" to facilitate cyclisation. Furthermore, the great reactivity of the thiophen ring can be utilised for the introduction of substituents§, as well as for effecting the process of cyclisation itself, in which a hydrogen atom of the thiophen ring acts as the second functional group.

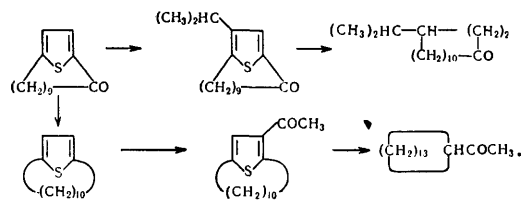
‡ Disregarding for the moment actual methods of effecting the required changes, we can readily imagine the use of various bi- and poly-cyclic systems containing other heterocycles instead of thiophen rings, *e.g.* furan, for the preparation of higher cycloalkane derivatives. However, as far as the Reviewer is aware, no more convenient method of opening a heterocycle for preparative purposes exists other than reductive desulphurisation of thiophen compounds (for greater detail see the reviews in Refs. 308 and 309).

Let us illustrate this by an example: Winberg *et al.*[84] synthesised a tricyclic compound containing two furan rings (V, X = O), and in order to prove its structure converted it into cyclododecane. This was achieved by a four-stage synthesis: the initial compound was subjected to hydrogenolysis over copper chromite, the product acetylated, and the resulting mixture of acetates converted by pyrolysis into a mixture of cycloalkenes, which on hydrogenation over platinum oxide gave the required cyclododecane. If this were a matter of preparing the alicyclic hydrocarbon from the tricyclic system, such a route could hardly be convenient. Nevertheless, if we start from the analogous tricyclic system containing two thiophen rings (V, X = S), conversion into cyclododecane can be accomplished by the action of Raney nickel in one operation.

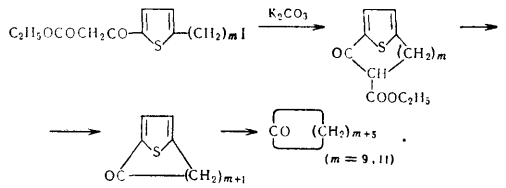


Thiophen can be used in another way for the synthesis of macrocyclic compounds: bifunctional long-chain aliphatic compounds can be obtained by reductive desulphurisation of its derivatives, and the former can then be subjected to cyclisation by one of the known methods. In particular, higher aliphatic dicarboxylic acids and hydroxy-acids have been prepared from thiophen derivatives[310,311], their synthesis by other methods being difficult. However, this second type of use is less specific.

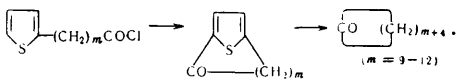
§ This possibility has been realised in the preparation of acetylcyclotetradecane and 4-isopropylcyclotetradecanone[312]:



Cyclisation can be accomplished by Friedel–Crafts acylation[294-296,299-301,305,306], Hunsdiecker intramolecular alkylation[297,298,304], and also acyloin condensation[294,303]. It must be noted, however, that the usual conditions of the acyloin condensation (fused sodium in boiling xylene) are unsuitable for the cyclisation of thiophendicarboxylic esters[294,313]. Success has been achieved[303] only by carrying out the reaction in a mixture of xylene and ether in the presence of a liquid potassium–sodium alloy at 50–60°. Nevertheless, application of the acyloin condensation in the thiophen series is subject to several serious limitations, which impede its use for the preparation of bicyclic systems containing the thiophen ring. In contrast, intramolecular alkylation enables the corresponding bicyclic β-keto--esters containing the thiophen ring to be obtained in high yields (up to 80%), from which the higher cycloalkanones — exaltone and dihydrocivetone — are obtained by ketonic cleavage followed by the action of Raney nickel[297,298,304]:



Intramolecular acylation of ω-thien-2-ylalkanoyl chlorides is especially interesting in that no open-chain bifunctional compound need be built up, since the free 5-position in the thiophen ring acts as the second function. Thus synthesis of the initial compounds is considerably simplified, and the aromatic character of the thiophen ring can be fully exploited. Cyclisation of the higher ω-thien-2--ylalkanoyl chlorides occurs with entirely satisfactory yields (around 60%). From the resulting products, α-cyclothienones, have been obtained cyclotetradecanone, exaltone, cyclohexadecanone, and dihydrocivetone.



Intramolecular acylation is carried out by the high dilution technique in chloroform, with aluminium chloride–ether as condensing agent (for further details see Refs. 306 and 314). Study of the intramolecular acylation of ω-thien--2-ylalkanoyl chlorides reveals a definite effect of the heterogeneity of the medium on the direction of the process, resembling the effect of the surface area of metallic sodium in the case of acyloin condensation. The yields of α-cyclothienone have been found[306] to increase not only with rise in concentration of the condensing agent, which is fully expected, but also at moderate concentrations in the presence of a solid adsorbent, for which purpose aluminium oxide, silica gel, and a product of the incomplete hydrolysis of the aluminium chloride–ether compounds have been used. This effect can be assumed to be due to adsorption of the molecules undergoing cyclisation, and is of general value in various types of cyclisation reaction.

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At the present time the development of synthetic methods makes possible the preparation in quite high yields of the most diverse macrocyclic compounds. Owing, however, to the specific peculiarities and limitations inherent in almost any method of synthesis, the preparation of macrocyclic compounds remains a fairly complicated task. It is difficult to assess the relative value of a particular method, especially in view of the rapid development of this field. Nevertheless, it may be assumed that methods of synthesising macrocyclic compounds "with a transannular bond" will be increasingly developed and applied during the next few years. At present these methods are widely used for obtaining compounds of medium ring size, mainly eight-, ten-, and twelve-membered alicyclic compounds, *i.e.* the particular group of macrocycles which is least readily obtained by cyclisation methods. There can be no doubt, however, that with further development the principle of synthesis with transannular bond, excluding cyclisation with formation of a thermodynamically unfavourable ring, will be extended to the range of large rings[247]. In this connection it is relevant to mention that this principle perhaps underlies the biosynthesis of macrocyclic natural products[315].

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LUMINESCENCE OF THE RARE-EARTH ELEMENTS AND ITS APPLICATIONS IN ANALYTICAL CHEMISTRY

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I. INTRODUCTION

Physical methods of analysis are now widely applied in analytical chemistry. In some cases, these are the only methods available: this is particularly true of the rare-earth elements (REE). These elements are so closely similar in chemical properties that analysis by conventional chemical methods becomes very difficult. Therefore they are usually analysed by spectroscopic methods, among which luminescence analysis is becoming increasingly important [1].

Analysis by emission spectroscopy [2], despite its generality, is also very difficult to apply to the REE, because the optical spectra of all the REE contain very many lines (of the order of thousands): unless the resolving power of the spectrograph is high enough, the lines of one element can be superimposed on those of another. The linear dispersion required is of the order of 1–2 Å.

Spectral analysis in the X-ray region of the spectrum is a better and more accurate method of analysis for REE, and is the most satisfactory method at present available. However, emission spectroscopic methods suffer from a relatively low sensitivity, reaching 10^{-3}% only in the most favourable case.

The similarity in chemical properties of the REE is known [3] to be due to the structure of the electron shells of the REE atoms: the inner 4*f* shell is progressively filled whilst the outer 5*s*, 5*p*, and 6*s* shells are already full, and this gives rise to the closely similar chemical properties.

The optical properties of the REE (light absorption and luminescence) are determined mainly by the 4*f* shell, and vary from element to element. Thus, they can be used to identify the individual elements. The screening of the inner 4*f* shell by the outer electron shells of the atom ensures that discrete spectra are obtained which are characteristic of these atoms, and makes the optical properties of the REE less sensitive to the surrounding medium.

II. LUMINESCENCE OF THE RARE-EARTH ELEMENTS

1. Luminescence of Pure Salts and Their Solutions

The optical properties of the REE are described in detail in a book by El'yashevich [3].

The absorption spectra of the REE, whether as crystals of the pure salts or in solution, are characterised by narrow bands in the infrared, visible, and ultraviolet regions of the spectrum. Wide bands, merging into a continuum, can be observed in the far ultraviolet. The discrete spectra of the REE ions are associated with quasi-forbidden transitions within the 4*f* shell: this is confirmed also by the small values of oscillator strength (f), of the order of 10^{-6}–10^{-8}. The continuous absorption in the ultraviolet must be ascribed to electronic transitions from the 4*f* shell to outer shells, which are strongly affected by the surrounding medium.

The luminescence spectra of REE situated in the middle of the group (Sm, Eu, Gd, Tb, Dy) also consist of a series of narrow bands. As in the case of the absorption spectra, this is due to transitions within the 4*f* shell. The lifetime in the excited state (τ) of these elements is high [4], of the order of 10^{-2}–10^{-4} s.

Systematic data on the absorption of REE ions in aqueous solution have been available since the work of Prandtl and Scheiner [5]. The absorption spectra show a systematic trend: the elements situated at the beginning and at the end of the REE group (except Ce and Yb) have absorption bands in the long-wavelength region of the spectrum, which gradually shift towards shorter wavelengths with elements lying near the middle of the group. Gadolinium absorbs only in the ultraviolet: this is because the ground level from which energy transitions occur during absorption shifts to a deeper position as we move towards gadolinium.

Unlike many other inorganic substances, which show luminescence only in the solid state, REE salts luminesce also in solution, retaining their characteristic spectrum.

The fluorescence and absorption spectra of triply charged REE ions, in solution or in the form of pure salts, were investigated systematically by Zaidel' and coworkers [6-9] and by many foreign workers [10-15].

The luminescence spectra of elements near the middle of the group (Sm, Eu, Gd, Tb, Dy) retain their line character even in solution. The elements at either end of the group have more diffuse spectra. In crystals, the bands are somewhat narrower, and are usually split into separate lines according to the strength and symmetry of the electric field in the crystal.

The structure of the luminescence bands, like that of the absorption bands, is slightly affected by the environment of the REE ion in solution or in the crystal (solvent effect in solution, and effect of crystal structure and of the anion in crystals). The pH of the medium has a particularly large effect on the luminescence. There is an optimum pH value for each system, giving maximum luminescence.

Both the upper and the lower energy levels are altered when the interaction between the ion and its surroundings increases. Since the upper levels usually suffer a greater shift, the spectrum is usually displaced towards longer wavelengths. The band structure is more clearly revealed at low temperatures, when both the resolution and the intensity of the bands are improved by the decreased energy fluctuations.

Luminescence can be induced in the REE by absorption in narrow spectral bands, and also by absorption in wide bands merging into a continuum in the ultraviolet region of the spectrum. The position of the luminescence bands is independent of the method of excitation (photoexcitation, or other kinds of excitation such as cathodic, X-rays, etc.). However, the intensity of bands can vary quite considerably, owing to the different quenching probabilities of different states of the ion, and also to the variation of the absorption coefficient of the ion with the wavelength of the exciting light.

Work on the luminescence of REE has been mainly directed, in recent years, towards interpreting the absorption and luminescence spectra of REE in pure salts and in solutions, and also towards studies of the effect of electric and magnetic fields on the energy state of the ions [16-30].

Many papers give new experimental results on the luminescent properties of REE. The absorption spectrum of promethium in solution (98% D_2O) has been determined [31] between 3000 and 8300 Å. It consists (Fig. 1) of various groups of lines, the most intense of which occur at the wavelengths 7347, 7019, 6838, 5679, and 3281 Å. The

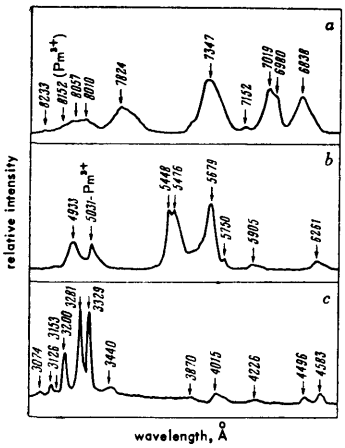

Fig. 1. Absorption spectrum of promethium in solution.

same authors have also reported[32] the luminescence spectrum of $PmCl_3$. This compound is self-luminous because of the high β activity of Pm. Under the influence of ultraviolet radiation its fluorescence increases as a function of the intensity of the exciting light. The fluorescence spectrum of $PmCl_3$ contains groups of lines around 4610, 4980, 5410, 5900, 6600, 7420, and 8300 Å. Several papers deal with the luminescent properties of Gd[33-35] and Tb[36-38].

The fluorescence of some REE can be observed in very dilute solutions[39-42] by using short-wavelength excitation (2000–3000 Å).

The Table gives the wavelengths of the most intense fluorescence bands, the minimum concentrations of the element, and the most effective excitation light sources for a number of REE ions in solution (Ce, Eu, Gd, Tb).

It should be noted that satisfactory results can be obtained only if the salts and the solvent (water, alcohol) are very pure. The Eu^{3+} ion is exceptional, because it does not fluoresce in a pure solution: SO_4^{2-} ions must be present to cause fluorescence of Eu^{3+}.

The intensity of fluorescence at low REE concentrations ($< 0.1\%$) is proportional to the amount of fluorescing element in solution. This property can be used for the quantitative estimation of REE in solution.

It can be seen from the Table that fluorescence analysis offers unsurpassed sensitivity for Ce, Gd, and Tb. The precision of the method depends very much on the procedure used to record the spectrum, and can be as high[41] as 1–2%.

2. Luminescence of Crystal Phosphors Activated by Rare-Earth Elements

Crystal phosphors[43,44] provide intense fluorescence with a characteristic line spectrum even with many of the other REE, *e.g.* Pr, Nd, Pm, Ho, Er, Tm. In this case the REE play the role of activators — a minor constituent, incorporated into the main substance, which determines the nature of the light emission from the phosphor. The photoluminescence of crystal phosphors can be induced either through light absorption by the activators themselves

TABLE.

REE	Exciting source	Min. REE concn., %	λ, analytical, Å	Remarks
Ce	Fe spark	10^{-7}	3130—4070	aqueous solution[6]
Pr	Ni spark	$5\cdot10^{-3}$	6400	crystal phosphors[64]
Pr	cathode rays	$5\cdot10^{-5}$		crystal phosphors[88]
Nd	cathode rays	$5\cdot10^{-4}$	10800	crystal phosphors[88]
Sm	W spark	10^{-5}	5680 6100	crystal phosphors[91]
Eu	Fe spark	10^{-2}	5930 6160	aqueous solution[35]
Eu	cathode rays	10^{-4}		crystal phosphors[88]
Eu	Hg lamp	10^{-4}	6130	organic complexes[107]
Eu	W spark	10^{-5}	5930	crystal phosphors[91]
Gd	cathode rays	10^{-4}	3110	crystal phosphors[88]
Gd	W spark	10^{-6}	3130	crystal phosphors[91,92]
Tb	Ni spark	10^{-6}	5450	aqueous solution[7]
Tb	Hg lamp	10^{-3}	5450	organic complexes[107]
Tb	cathode rays	$5\cdot10^{-4}$		crystal phosphors[88]
Tb	Ni spark	10^{-5}	5430	crystal phosphors[69]
Dy	cathode rays	$5\cdot10^{-4}$		crystal phosphors[88]
Dy	Ni spark	10^{-4}	5760	crystal phosphors[69]
Ho	Ni spark	10^{-4}	5500	crystal phosphors[69]
Er	cathode rays	10^{-3}	5200—5500	crystal phosphors[88]
Tm	Ni spark	$5\cdot10^{-3}$	6540	crystal phosphors[69]
Tm	cathode rays	10^{-3}		crystal phosphors[88]
Yb		10^{-4}		crystal phosphors[128]

or by transfer to the activators of the radiant energy absorbed by the main constituent. Luminescence in these systems requires that the host material should be in the crystalline state: for this reason, the phosphors are subjected to heat-treatment. The host lattice for REE crystal phosphors may be provided by the oxides, sulphides, fluorides, sulphates, silicates, phosphates, tungstates, and molybdates of metals of Groups II–IV of the Periodic Table. REE phosphors having well-defined line spectra can be obtained with host materials in which the ionic radius of the cation is comparable with that of the activator. Under these conditions, activator ions can be introduced into the host crystal by isomorphous substitution. The most effective hosts for REE are found experimentally to be calcium tungstate and calcium fluoride.

The properties of crystal phosphors activated by REE, the features of their luminescence, and the nature of the luminescence centres form the subject of a continuing investigation by Feofilov[45-54], who has made a special study of Ca, Ba, and Sr fluorides, and by other workers[55-87].

Feofilov's work (based on the polarisation method) leads to the conclusion that large numbers of luminescence centres are present, and makes it possible to link the various types of centre with certain preparative conditions (in particular, the charge of the activating ion may vary according to the conditions of synthesis)[52,53]. The luminescence spectrum and the value of τ depend on the charge of the activator ion. Double charged REE ions, unlike the triply charged ions, are characterised by wide bands and low values[49,51,53] of $\tau(\sim 10^{-6}$ s).

A review by Feofilov[52] gives a chart of the spectral regions in which luminescence bands of the individual REE ions have been observed in crystals of fluorite CaF_2. This chart (Fig. 2) is reminiscent of Prandtl's scheme for the absorption spectra of the REE. The luminescence spectra also show some regularity, though possibly less marked, in the location of the bands corresponding to the various REE ions. For ions close to the beginning or the end of the REE group the luminescence spectra are displaced towards long wavelengths, whereas the luminescence of Gd occurs only in the far ultraviolet.

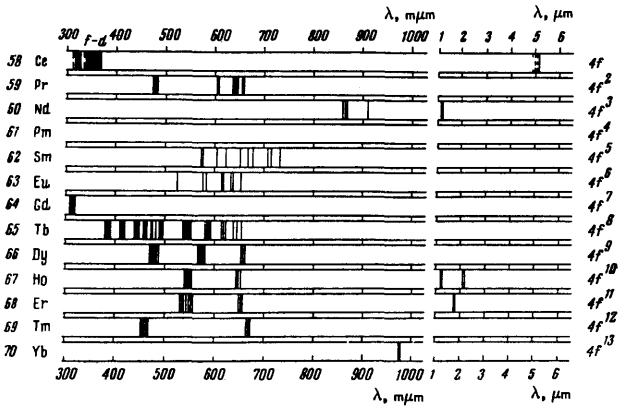

Fig.2. Schematic chart of the luminescence spectra of REE ions in CaF_2 crystals.

Many of the papers already mentioned[55,58,60] deal with the properties of phosphors based on the sulphides or oxides of alkaline earth metals activated by REE. There are also some papers[61,66,67] on the cathode luminescence of crystal phosphors activated by REE.

A paper by Trofimov[62] on the diffusion of REE activators in various crystals contains some very interesting results from the point of view of analytical chemistry. He puts forward a scheme (Fig. 3) showing the direction of diffusion of REE from one crystal to another — the "acceptor" crystal — at high temperatures. The best acceptors for REE are, according to Trofimov, ThO_2 and $CaMoO_4$, which become excellent crystal phosphors in the presence of REE. Fig. 4 shows the luminescence spectrum of one of the crystal phosphors based on ThO_2.

The luminescence spectra and intensity depend on both the nature and the concentration of the activator, and also on the nature of the substrate. The thermal history of the sample (temperature and time of heat-treatment) also plays an important role. The position of the bands in the luminescence spectrum of a phosphor activated by a given REE is practically independent of these factors, but the structure of the bands does vary.

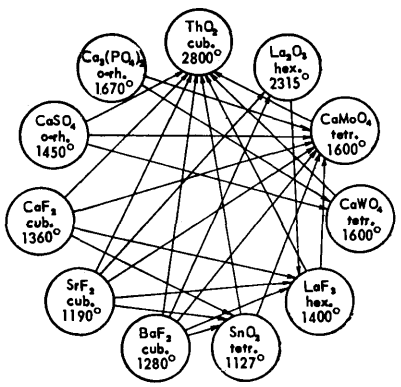

Fig.3. Scheme showing directional diffusion of activator when a mechanical mixture of two crystalline substances is heated (melting points indicated in circles).

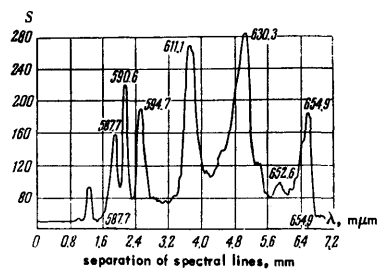

Fig.4. Luminescence spectrum of ThO_2–Eu.

The mode of splitting of the levels, which determines the type of spectrum obtained, is related to the crystal lattice and its symmetry, which in turn dictates the symmetry of the electric fields to which the luminescence centre is exposed.

The effect of the crystal lattice on absorption and emission spectra is shown in: (1) displacement of individual lines and groups of lines, related to changes in lattice parameters; (2) splitting of individual lines, determined by the symmetry of the surrounding electric field, *i.e.* by the symmetry of the crystal lattice of the host material of the phosphor (the number of components into which splitting occurs is higher the lower the symmetry of the field); (3) change in intensity of the lines for different crystal structures; (4) the appearance of new lines, caused by the superposition of vibrational levels of the host lattice itself upon the fundamental electronic transitions; and (5) line broadening, due to the possibility of an irregular arrangement of atoms in the crystal about the radiating ion, leading to random electric fields around the luminescence centres (non-isomorphous introduction of the activator into the lattice).

As was pointed out in the foregoing, these effects can be observed also in the pure salts, which can be regarded as phosphors with a high concentration of activator. The variation of luminescence spectra with the nature of the surroundings, which is an obstacle to the application of luminescence analysis in analytical chemistry, may be used to solve many problems in crystal chemistry, such as: (1) detection of incipient formation and decomposition of solid solutions; (2) identification of crystal lattice types; (3) recognition of polymorphic transformations; (4) demonstration of detailed features in the microstructure of crystals; (5) detection of microdefects in a crystal, and elucidation of their nature; (6) monitoring the formation of mixed crystals; (7) distinguishing the amorphous and the crystalline states of the material; and (8) the study of diffusion in the solid phase.

Several problems in crystal chemistry have been successfully solved by Trofimov[69] using the luminescence spectra of REE.

However, it is possible to use the luminescence spectra of REE for the analysis of these elements when present in the same external medium, *i.e.* when the REE are introduced into a host of a given composition under identical conditions.

Servigne published a series of papers[88] on luminescence analysis, in which he showed that the luminescence of REE can be detected at very low concentrations if calcium tungstate or molybdate is used as the host material. Some of his data on the minimum concentrations of REE activators

(Pr, Eu, Gd, Tb, Dy) are reproduced in the Table. For activator concentrations below 0.1% the luminescence intensity is usually proportional to the amount of activator (other conditions being equal). The luminescence of REE can therefore be used as a quantitative method of analysis either in liquid or in solid solutions (crystal phosphors).

It is important to remember, however, that impurities can have an effect, and that two or more activators can interact[70,84-87], when mixtures of elements are being determined. The computational difficulties of allowing for the various factors which affect the luminescence intensity have so far militated against the widespread use of the luminescence of crystal phosphors in quantitative analysis.

Very few papers on this topic have been published to date[89-96], but their importance is undeniable.

The determination of Gd, Eu, and Sm in thorium, and of Gd in beryllium, has been described[91,92]. The extremely bright luminescence of REE phosphors based on ThO_2 allows the determination of Gd, Eu, and Sm in thorium at the 10^{-5}% level with an accuracy of 20–50%. The high sensitivity (10^{-6}%) of the luminescence method of determining Gd in beryllium[92] was also achieved with the help of ThO_2, by utilising the phenomenon of the thermal diffusion of REE activators in crystals as indicated above.

Impurity effects can be avoided[89-92] by using the method of small additions. This consists in preparing a series of phosphors with the same host but containing different, known amounts of the activator element to be analysed. The intensities of the analytical line in the fluorescence spectrum are used to construct a graph, from which the unknown concentration of the element is read off. The additions should be comparable with the unknown concentration (assumed to be small) in order to avoid departures from linearity between fluorescence intensity and activator concentration.

The REE can be detected qualitatively in minerals by comparing the absorption or luminescence spectra of the samples with those of synthetic compounds of the same composition and containing REE additions. Work of this type has been reported by Feofilov[53], Przibram[97], and Trofimov[98].

Feofilov[53] and Przibram[97] have studied the nature of the coloration and luminescence of fluorite. Trofimov[98] has investigated the luminescence of zircons, and has been able to show that the line spectra in the visible region and in the ultraviolet are due to the presence of Dy and Gd respectively.

These papers[53,88-98] clearly illustrate the way in which the luminescence of crystal phosphors can be used in analytical chemistry. The method is suitable, in principle, for the analysis of all REE: however, the host crystal of the phosphor must be chosen so as to give maximum luminescence of the REE activator if the highest sensitivity is desired.

A disadvantage of the method is its great laboriousness, arising mostly from the need to exclude impurities, which entails complicated chemical manipulation.

Furthermore, as in the case of pure salts and solutions, short-wavelength ultraviolet radiation provides the most effective excitation of the luminescence of REE phosphors. Thus, the excitation source must be a spark with suitably chosen electrodes, which adds to the difficulty of the analysis.

Some authors have used a rapid method of preparing[93,95,99,100] REE crystal phosphors, by means of borax or NaF beads. However, the bead method has a much lower analytical precision.

3. Luminescence of Inner Complexes of Rare-Earth Elements

Organic inner complexes of the REE, which have recently been discussed in a number of papers[101-123], are of considerable interest. These investigations primarily aim to identify the mechanism whereby the energy of the exciting light is transferred from the organic part of the complex to the REE ions.

The organic compounds on which REE inner complexes are based absorb strongly in the range 200–400 mμm. When the complex is formed the absorption spectrum shifts a little further in the direction of longer wavelengths. Irradiation of some REE complexes (Eu, Sm, Tb, and Dy) in the near ultraviolet (*e.g.* $\lambda = 365$ mμm) produces strong luminescence of the REE, caused by transfer to the REE of the radiant energy absorbed by the organic part of the complex. Kuznetsova[107] has shown that the efficiency of energy transfer is high at low temperatures, when the probability of radiationless transitions is small.

The photoluminescence spectra of REE inner complexes (Fig. 5) retain a discrete structure and are not substantially different from the spectra of simple salts of these

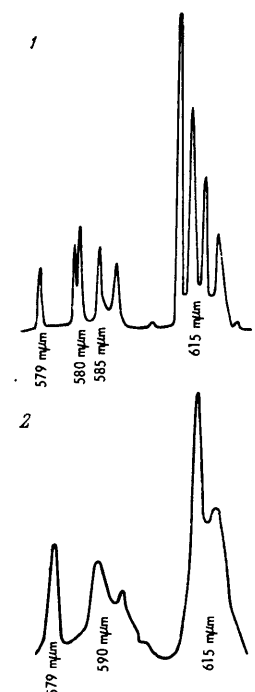

Fig.5. Luminescence spectra of the crystalline complexes of europium with:
1) ethylenediamine-2-hydroxy-naphthaldehyde;
2) ethylenediamine-5-nitrosalicyl-aldehyde.

elements in the crystalline state. The energy distribution in the spectrum and the type of splitting depend on the nature of the organic ligand.

The inner complexes exhibit luminescence both in the crystalline state and in solution provided that the resonance level of the REE ion is the lowest excited level of the whole system (Fig. 6), since only thus can energy transfer take place from the organic ligand to the REE ion. The resonance level of the Eu^{3+} ion is situated below all possible energy states of the complex, and therefore its spectrum is observed in the emission of practically every one of the complexes investigated, in solution as well as in the crystalline state, whereas the Gd^{3+} ion is not excited in any of the complexes because its resonance level is too high.

Since the energy state of the ion varies somewhat with the surrounding medium, it is sometimes found that the ions fluoresce only under certain conditions. For example, Sm, Tb, and Dy show luminescence only in some complexes. Samarium luminesces satisfactorily when complexed with ethylenediaminesalicylaldehyde. The luminescence of Tb can be observed by complexing it with phenyl salicylate (salol), the resulting complex luminescing only in solution. For Dy the complexes with *o*-phenanthroline and 2,2′-bipyridyl can be used. These latter complexes can be employed for the simultaneous analysis of all four REE elements mentioned above, including Sm. When Pr, Nd, Er, Ho, Tm, and Yb are present in complex compounds, emission occurs in the infrared.

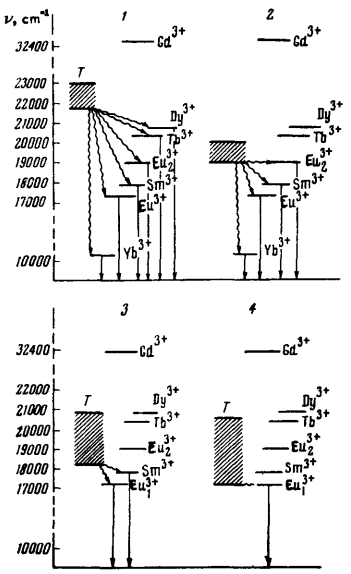

Fig. 6. Energy diagram showing how the energy of the exciting light is transferred from the organic ligand to the REE ion (the wavy arrows tentatively denote energy transfer from the lower level of the excited state of the organic ligand *T* to an excited level of an REE ion), energy being transferred to:
1) all the ions except Gd^{3+};
2) only Eu_2^{3+}, Sm^{3+}, and Yb^{3+};
3) only Sm^{3+} and Eu_1^{3+};
4) only Eu_1^{3+}.

In most cases, the luminescence of complexes can be observed only at low temperatures: only Eu gives good luminescence at room temperature. The work of Poluektov and coworkers [120,121] has shown that the luminescence intensity of REE can be enhanced by using ternary complexes with two different ligands able to transfer energy to the REE ion. Inner complexes of REE are easy to prepare, and the use of these materials therefore simplifies the luminescence analysis of REE, particularly since their luminescence can be excited by long-wavelength ultraviolet radiation from a mercury lamp.

The sensitivity of the method is fairly high, allowing, for example, Eu and Tb to be determined down to 10^{-4}% and 10^{-3}% respectively.

Papers on the use of the luminescence of REE complexes for analysis are not very numerous [119-123], but they provide adequate examples.

Neunhoeffer [124] has described an entirely different method of observing the luminescence of REE. The element to be analysed is mixed with calcium oxide, and the mixture is introduced into a hydrogen flame: strong luminescence is excited by the slow electrons present in the hydrogen flame. This procedure makes it possible to observe the luminescence of elements such as Y and La, which do not normally luminesce. The method is very sensitive, the author claiming that luminescence can be observed even at a concentration of Y as low as 10^{-6}%.

We may conclude, therefore, that the luminescence analysis of REE has an important role to play. In spite of some unfavourable features (such as the need to remove interfering impurities), the luminescence method for the analysis of REE merits close attention. With some elements (Eu, Sm, Gd, Tb, Dy), whose luminescence is very easily observed in nearly all the examples discussed in the foregoing, the procedure is already clear enough, and only remains to be introduced into everyday practice. For the other elements, further work is needed to find the simplest and most effective ways of observing the luminescence.

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GAS–LIQUID CHROMATOGRAPHY OF LIPIDS

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I. INTRODUCTION

Lipids and their component aliphatic alcohols, aldehydes, and acids form one of the most complex groups of naturally occurring compounds; for this reason, over the past few decades workers in many countries have used various types of chromatography such as adsorption, displacement, partition, and reversed-phase chromatography to study these compounds. Our ideas on the structure and metabolism of lipids in the living organism have been greatly extended by the use of these methods. However, there are many disadvantages associated with their use in lipid chemistry: much time is required to get a satisfactory separation, the analysis is not sufficiently reproducible, it is laborious, the distribution parameters for unsaturated and saturated lipids overlap, etc.

In the search for methods of effectively separating complex mixtures of lipids from the animal body, that sometimes contain as many as 60 components, the English biochemists James and Martin discovered in 1952 an entirely new type of chromatography, gas–liquid chromatography[1]. In this method separation of the mixture is based on the different distribution of the components between two phases, a stationary liquid phase supported on a solid carrier forming

the chromatographic column and a gas passing through the column. At pressures around atmospheric, gases have much lower densities and viscosities than liquids, and the resistance of the column to the gas stream is relatively low. This permits very rapid analysis with a highly effective separation, which is ensured by the rapid mass exchange on the surface of the stationary phase. The concentration of organic vapour issuing from the column may be recorded continuously by an automatic device measuring a particular physical property. The advantages of gas–liquid chromatography have given it a leading position compared with other types of chromatography. This review does not contain a detailed presentation of the principles of gas–liquid chromatography or a description of chromatographic apparatus; for these the reader is referred to a number of books [2-9].

Gas–liquid chromatography is used to separate methyl esters of fatty acids, the free acids, alcohols, aldehydes, ketones, amines, nitriles, hydrocarbons, and to some extent triglycerides, derivatives of mono- and di-glycerides, etc. It is the best method of separating and quantitatively determining the compounds mentioned. The method has also been used for the study of long-chain aliphatic radicals (residues of acids, alcohols, aldehydes, etc.), which enter into the composition of non-volatile lipids — waxes, phospholipids, glycolipids, sulpholipids, lipoproteins, etc. During the past ten years a large number of experimental studies in lipid gas–liquid chromatography have been made and a number of reviews have appeared [10-17].

Our aim in the present review is to describe the present state of this very topical problem. Numerous papers in which gas–liquid chromatography was used only for lipid analysis, with no original work on the theory or technique of the method, have not been covered. Papers dealing with studies of short-chain (to C_8) aliphatic compounds, sterols, essential oils, and other isoprene derivatives are hardly touched upon. The review covers the most important papers on gas–liquid chromatography of the methyl esters of fatty acids, the free acids, glycerides, and some other lipids, published up to 1st July 1963.

II. GAS–LIQUID CHROMATOGRAPHY OF METHYL ESTERS OF FATTY ACIDS

1. Conditions for Separating Methyl Esters

In the first gas-chromatographic studies to determine the acid composition of lipids, chromatography of the free fatty acids was used [1]. However, in 1953 it was found that use of the less polar methyl esters has a number of advantages: a more effective separation is achieved at a lower temperature in a shorter time, and more precise results are obtained in identification and quantitative determination [18,19]. At present, gas–liquid chromatography of the methyl esters of higher fatty acids is the standard method for investigating the composition and structure of natural and synthetic lipids [20]. The method covers the most diverse fatty acids in the C_1–C_{30} range and higher, including saturated, branched, and unsaturated acids (*cis*- and *trans*-isomers), hydroxy-acids, epoxyketo-acids, etc. By modern methods all these acids can be converted rapidly and quantitatively into methyl esters. The esters obtained are separated on columns filled with adsorbent, or capillary columns, heated to 150–300°; the column is packed with a solid carrier (usually kieselguhr) on which is a high-boiling non-polar or polar liquid phase. Nitrogen, helium, or argon is used as the carrier gas, which passes through the column at 30–100 ml min^{-1}. The methyl esters are detected and quantitatively determined by means of a katharometer or an ionisation detector. Table 1 gives some examples of the separation of methyl esters.

TABLE 1. Gas–liquid chromatography of methyl esters of higher fatty acids.

Solid carrier	Liquid phase and its content	Temp., °C	Carrier gas	Gas flow, ml min^{-1}	Detector	Composition of sample and duration of analysis, min	Ref.
Sterchamol 52–85 mesh	Silicone DC	210	N_2	5.5	katharometer	C_8–C_{24}	21
Celite 545 50–100 μm	Apiezon L, 10–20%	197–231	N_2	20–30	»	C_{12}–C_{28} 80–180	22
Celite 545 100–210 mesh	Apiezon L, 20%	197	Ar	60	ionisation	C_{12}–C_{28} 72	23
Ditto	poly(ethylene glycol adipate), 24%	180	Ar	40	»	C_{12}–C_{18} 70	23
Celite 545 140–170 mesh	poly(ethylene glycol succinate), 20%	203	He	200	katharometer	C_{10}–C_{26} 38	24
Capillary column 30–60 m × × 0.25 mm	Apiezon L	200	Ar	0.5–1	ionisation	*cis-trans*-isomers of methyl linoleate and methyl linolenate, 60	25
Ditto	poly(diethylene glycol succinate)	168–188	Ar	0.5–1	»	ditto, 40	25

The synthesis of the methyl esters, the chromatographic separation conditions, and also the methods of their identification, quantitative analysis, and determination of radioactivity are considered in detail below.

2. Synthesis of Methyl Esters for Chromatographic Separation

At present there are two methods of synthesising methyl esters of fatty acids for chromatographic purposes: (*a*) catalytic transesterification of lipids in methanol solution; and (*b*) saponification of the lipids and esterification of the free fatty acids.

(*a*) Transesterification of fatty acids. The lipids are dissolved in absolute methanol; if they are not completely soluble, benzene or toluene is added [26]. To ensure a quantitative yield of esters, all the reagents must be carefully purified [27]. Reaction conditions used by different workers are given in Table 2. This shows that methanolysis is completed much more rapidly in a basic medium than in an acidic one; HCl and H_2SO_4 have about the same catalytic activity, but K is much more active than

TABLE 2. Conditions for transesterification of triglycerides in methanol.

Catalyst	Duration, h	Temp., °C and gaseous medium		Yield of esters, %	Ref.
5% HCl	2	64–65	air	—	28
0.8 *N* HCl	2	64–65	air	—	23
5% HCl	2	80–100	air	95	26
5% H_2SO_4	18	64–65	air	—	29 *
0.005% Na	0.5	—	—	96	30
0.1 *N* Na or K	1.5–2	64–65	N_2	98	31 *
1% Na	2 min	60	N_2	99	32

* Methanolysis of phospholipoids and sterol esters.

Na.[31] In a 1% solution of Na in primary alcohols, alcoholysis of triglycerides is completed in 2^m min, where m = = 1–6 is the number of carbon atoms in the alcohol molecule[32]. Methanolysis of phospholipoids and sterol esters requires more time and a larger excess of methanol and catalyst than does the methanolysis of triglycerides. Final purification of the methyl esters before chromatography may be achieved by fractional distillation[33], vacuum sublimation[26,34], adsorption chromatography on a silic acid column[31], or thin-layer chromatography[32]. The methyl esters obtained must be fully protected from oxidation; they can be kept for long periods in benzene solution below 0° in the dark under an inert gas[35].

(*b*) Esterification of free fatty acids. Transesterification conditions are quite suitable for the esterification of fatty acids obtained by saponification of lipids[36]. However, there are more rapid methods of esterification that require only a few minutes[15,16]. For a number of years methyl esters have been prepared by esterifying fatty acids with diazomethane[37]. Previously the danger of handling diazomethane and the possibility of the formation of pyrazolines by addition of CH_2N_2 to the double bonds of fatty acids[26] were considered disadvantages of this method. It has recently been found that when a freshly prepared solution of CH_2N_2 in a mixture of CH_3OH and ether (1 : 9) is used, the methyl esters are obtained in quantitative yield in 10 min, free from decomposition and polymerisation products; the methanol in this reaction appears to act as a catalyst[38]. It has also been recommended[39] that the esters should be synthesised by keeping the fatty acids in a weak solution of diazomethane at -34° for $2\frac{1}{2}$ days. Esterification of fatty acids in a solution of boron trifluoride in methanol is complete in only 2 min, but the yield of methyl esters does not exceed 80–85%; epoxy-acids and acids with conjugated double bonds cannot be esterified by this method[40]. In the formation of esters of higher fatty acids, CH_2N_2, HCl, and BF_3 show very similar activities[35,41]. To ensure a quantitative yield of the more volatile esters of the lower acids (C_1–C_{10}) diazomethane[41] should be used with docosane as solvent[42], or the ethyl esters may be prepared instead of the methyl[43].

The reaction with 2,2-dimethoxypropane in acidified methanol has been successfully used for the synthesis of methyl esters of 2-hydroxy-acids from cerebrosides and the esters of the acetates of these acids[44,45]. Aliphatic epoxy-acids are destroyed on saponification, being converted into the corresponding dihydroxy-acids; if epoxy--acids are present in lipids, methanolysis in sodium solution should be used[46].

There are other methods of synthesising esters. Hydrogenolysis of triglycerides with lithium tetrahydroaluminate gives free glycerol and LiAl alkoxides of the higher alcohols corresponding to the individual fatty acids. The acetylation products of these compounds — triacetin and acetates of fatty alcohols — have been determined by gas–liquid chromatography[47]. The reaction of silver salts with methyl iodide in an inert gas for 8 h has been proposed for the preparation of esters of volatile and non-volatile organic acids; the yield of methyl esters was 96–100% with this method[48].

3. Introduction of Sample and Temperature of Separation

Volatile components in the liquid phase and water vapour are removed from the column by maintaining it at 5–10 deg above the working temperature for 48–96 h and streaming carrier gas through it[24]. Sometimes the column with the solid carrier containing 10–50% of liquid phase is stabilised by being heated to 300° at a pressure of 10 mmHg for 5 h.[6]

The sample is introduced into the column as rapidly as possible, preferably without interrupting the carrier-gas stream. If only a small amount of material is available for analysis, the sample is dissolved in volatile organic compounds of the methyl tridecanoate type[23]. A device has been described for introducing small samples of methyl esters into a chromatographic column with a closed injection system[49].

Before the chromatographic separation commences, the methyl esters introduced into the column that are liquid or solid at ordinary temperature must be vaporised[15,16,46,50]. For this purpose, many chromatograph models are equipped with vaporisation chambers maintained at a temperature 50–100 deg above that of the column[24]. With capillary columns this temperature difference may reach 150 deg[25,51]. If the vaporisation of the sample at the entrance to the column is not instantaneous, the effectiveness of the separation is reduced, especially with components having a large retention volume V_R.[49] Esters of saturated and unsaturated acids are not usually affected by vaporisation[52]. However, unsaturated acids with conjugated double bonds and hydroxy--groups may undergo *cis–trans* isomerisation or dehydrogenation[53] in the vaporisation chamber. Esters of tung-oil acids, containing over 70% of elaeostearic acid, polymerise in the chromatographic column at high temperatures[15].

Correct selection of the working temperature and its control throughout the experiment determine the effectiveness of the separation and the accuracy of the quantitative determination of fatty acids. Sometimes a high column temperature is achieved by means of a vapour bath using high-boiling liquids such as polyethylene glycol (b.p. 197°)[22], but more often an air thermostat is used.

The temperature conditions for gas-chromatographic separation depend on the composition of the methyl esters in the sample and on the chemical nature of the liquid phase in the column. The best separations of aliphatic esters up to and including C_{30} on non-polar liquid phases (Apiezon M and L, Silicone) are achieved with a column temperature of 250–300°.[16,21,54] At still higher temperatures the rate of analysis increases, but the separation is less effective[23,25]. With polyester phases, the threshold temperature seldom exceeds 200–210°;[16,39,43] further heating may result in removal of liquid phase from the column, which would spoil the detector[55]. On capillary columns the same mixture can be separated at a temperature 40–50 deg lower than on columns packed with sorbent[12,25,56,57].

The temperature of the column has a considerable effect on the volume of the separate components retained. Thus methyl oleate and methyl stearate are not separated on a polyester column at 125°, but at 158–168° a good separation is achieved[12]. The "separation factor" (ratio of retention volume V_R of a component to that of the preceding component[58]) decreases with increasing working temperature for esters of saturated and branched-chain fatty acids; for unsaturated esters it increases (relative to the preceding saturated esters)[57]; this behaviour may be used for the chromatographic identification of fatty acids. When mixtures of methyl esters were being separated on a polar column without preliminary calibration of the katharometer an increase in temperature led to high results for readily volatile components and low results for esters with a high

retention time; as the temperature was lowered the divergence was largely eliminated[24,51] [see Section II, 8(*a*)].

If a mixture of methyl esters contains components differing markedly in volatility, it cannot be analysed at a single column temperature. In such cases the more volatile C_2–C_{10} esters are determined at 100–120°, and the esters of the higher fatty acids are separated at 180–200°; the esters of the lower acids emerge as one peak at the beginning of the chromatogram[15,58-60]. Recently chromatography of derivatives of lower and higher acids has been carried out with automatic programming of the working temperature of the column[15,61].

The katharometer should be carefully thermostatted to obtain reliable quantitative results[51]. The temperature of the katharometer is usually 25–75 deg above that of the column[24]. In some cases such a temperature gradient is set up for ionisation detectors[25,50].

The working life of a column is greatly increased if the temperature is reduced to 100° when it is not in use[11,25].

4. The Solid Carrier

In gas–liquid chromatography of lipids various kinds of kieselguhr (diatomaceous earth), such as Celite-545[22,30,62] or Chromosorb W[33,55,63-65] have been used most frequently; other materials used include Sterchamol[12], ground firebrick[46], glass beads[66], Embacel[34], and sodium chloride[19]. Carriers of particle size 50–150 mesh have been used in different investigations; the range of particle size in any column should not exceed 20 mesh. Before deposition of the liquid phase, the solid carrier is washed through successively with concentrated hydrochloric acid, KOH solution, NH_4OH solution, and water; it is then thoroughly dried[51,67]. Sometimes it is recommended that the column should be treated with dichlorodimethylsilane vapour[66,68,69], but this procedure may promote the retention of methyl esters on polyester columns[70].

Chromatographic columns can be packed with carrier containing the liquid phase by means of a vibrator and under pressure of the gas that is to be used in the separation[24,51]. In other cases packing is achieved by creating a vacuum inside the column[22].

The nature of the solid carrier considerably affects the separation of methyl esters; the esters of linolenic and arachidic acids are not separated with poly(ethylene glycol succinate) on Celite, but when the same phase is used on Chromosorb W, the arachidic ester appears on the chromatogram between the linoleate and linolenate peaks[71]. In contrast, the use of Chromosorb R and Celite-545 saturated with poly(vinyl acetate) gave similar results in the separation of artificial mixtures of methyl esters of fatty acids[66]. Considerable destruction of methyl *cis*-9,10-epoxyoctadecanoate on a column with silicone oil at 235° can be avoided by using Celite instead of firebrick C-22 as solid carrier[46].

Methyl esters of saturated and unsaturated acids may be adsorbed during separation on a column of Sterchamol or kieselguhr impregnated with a non-polar or polar liquid phase. Later the carrier gas desorbs the esters and sweeps them out of the column. Thus with Sterchamol 8% of the radioactivity of methyl [1-^{14}C]palmitate is eluted after the main peak. To reduce its adsorptive tendency Sterchamol was treated with hexamethyldisilazane or a 2% solution of sodium laurate, and kieselguhr was washed with hydrochloric acid and methanolic KOH. After such treatment only 4% of methyl [1-^{14}C]palmitate was adsorbed[72].

5. Chromatography on Non-Polar Liquid Phases

In work on the gas chromatography of methyl esters of higher fatty acids, high-boiling non-polar vacuum greases began to be used in preference to other liquids; these were organosilicon or paraffin in nature, *e.g.* Silicone DC 550, Apiezon M, Apiezon L, and polybutene[1,18,22,54,58,73].

The values of the retention volume of methyl esters are determined by differences in the partial pressure of the vapours of these compounds when they are dissolved in the liquid phase on the column; the partial pressure in turn depends on the nature and magnitude of forces of interaction between the molecules of the ester and those of the liquid phase.

At a vapour concentration of the organic compound in the gas stream of 3–5 $\mu g\ ml^{-1}$ or less, London dispersion forces are the only forces acting between the ester molecules and those of non-polar phases, and these forces weaken as the molecular weight is reduced and with branching of the aliphatic chain[23]. These phases ensure complete separation of esters of normal saturated acids differing in chain length by one carbon atom (separation factor 1.56) in the C_1–C_{34} range[58,74]. The retention time is comparatively large, and for methyl stearate it often exceeds 60 min. Esters of branched-chain acids emerge from the column before unbranched esters containing the same number of carbon atoms[14,23]; iso-forms of branched acids move more rapidly than the corresponding anteiso-forms[11,75,76]†.

Bromination is used before chromatography to separate esters of unsaturated acids: the brominated esters (except methyl oleate) are non-volatile at the separation temperature[58]. The chain length of an unsaturated acid can be determined by the preparative isolation of the ester with subsequent catalytic hydrogenation; the saturated ester obtained is identified by its retention volume[77]. Transesterification during hydrogenation with an Adams catalyst may be avoided by carrying out the reaction in methanol[78]. Other methods of identification are considered in Section II, 7(*b*) below.

In separations on non-polar fatty phases, the esters of unsaturated fatty acids are found on the chromatogram in front of the esters of the corresponding saturated acids. Saturated and monounsaturated esters are completely separated; di- and tri-unsaturated esters form a mixed peak, which is partly separated from the monounsaturated ester peak[79]. Separation of methyl linoleate and methyl linolenate was not achieved even on an Apiezon L capillary column of 200 000 theoretical plates[56]. When the distance between the carboxyl and the double bond is reduced, the retention volume V_R of monounsaturated esters increases somewhat[23,58]. The isomers of methyl linoleate — the 8,11-, 9,12-, 10,13-, and 11,14-octadecadienoic esters — have been partly separated on a polybutene capillary column[73]. Polyunsaturated esters with conjugated double bonds emerge from the column more slowly than do esters with isolated bonds[6]. The isomers of methyl linoleate

† In the iso-form of branched acids the aliphatic chain terminates in an isopropyl group, but in the anteiso-form it terminates in an isobutyl group. [An s-butyl group is probably meant here (Ed. of Translation).]

and methyl linolenate with conjugated bonds separate well on a column of Apiezon L; under the same conditions the above two esters themselves cannot be separated [34].

Non-polar liquid phases are used successfully to separate geometric isomers of unsaturated acids, formed by hydrogenation under industrial conditions; V_R for the *cis*-isomers of mono-, di-, and tri-unsaturated esters with isolated or conjugated double bonds is less than that of the corresponding *trans*-isomers [12,22,23,58,63]. The geometric isomers of methyl linoleate have been separated, on a capillary column of Apiezon L with an ionisation detector, into *cis-cis*, *cis-trans*, and *trans-cis* + *trans-trans* forms; methyl *cis-cis-cis*-linolenate moves in front of the *trans-trans-trans*-isomer. Geometric isomers of octadecadienoic acid with conjugated double bonds have also been separated [25].

Methyl *cis*-9,10-epoxyoctadecanoate from uredospores of a rust fungus has been separated from its acetylation product, the acetoxyhydroxyoctadecanoate, on a silicone column [46]. The separation of methyl esters of 2-hydroxy--acids has also been described [45].

At present non-polar liquid phases are mainly used for the preliminary fractionation of methyl esters according to the number of carbon atoms, for the determination of *cis*- and *trans*-isomers, and for comparative identification. Gas–liquid chromatography on polar liquid phases is now more often used to study the composition of complex fatty acid mixtures from natural sources.

6. Chromatography on Polar Liquid Phases

(*a*) Preparation of columns. Polar liquid phases were proposed for the separation of esters of saturated and unsaturated acids in 1958 [80,81]. The first polar phases, which consisted of derivatives of adipic acid — poly(ethylene glycol adipate) (LAC-1-296) and poly(oxyalkylene adipate) (Reoplex-400) — are still widely used. Polyesters of this kind $[-O-CO-(CH_2)_n-CO-O-]_m$‡ are synthesised by the polycondensation of succinic [30], adipic [23,82], and other dibasic acids with ethylene glycol or other polyhydric alcohol at 150–180°, usually in the presence of a catalyst (toluene-*p*-sulphonic acid, zinc chloride, etc.) in an inert atmosphere; the product is dissolved in alcohol or acetone, and purified from catalyst impurity and free acid by ion-exchange chromatography on Amberlite IR-120 or Duolite A-4. [30,65,67,70,73] The more thermostable high--molecular polyester fractions may be separated by reprecipitation from acetone solution with hexane [30]. The vapour pressure of the liquid phase at the working temperature should not exceed 0.5 mmHg. [83]

Poly(vinyl acetate) (Vinylite AYAC) with a molecular weight of 1500–23 000 is also used as a polar liquid phase. An advantage of this polymer is that on being heated it liberates only a small amount of acetic acid, which can be easily removed from the fractions collected in preparative work; under these conditions the noise level of the katharometer does not exceed 0.2 mV. [55] Decomposition of dimethyl malonate has occurred on poly(vinyl acetate) columns; when silicone oil was used no decomposition was observed [84]. In recent years acylated β-cyclohextrins have been used in the chromatography of methyl esters; these are characterised by low oxygen content, absence of terminal polar groups, uniform molecular weight, and thermal stability up to 236°. [85,86]

The polar liquid phase (5–25%) is added to the solid carrier, and the column material is conditioned as described above (Section II, 3). In this case the column must be stabilised with particular care, since the polyesters are unstable at high temperatures. If conditioning is not satisfactory or the temperature is too high, the liquid phase enters the detector and puts it out of action. Volatilisation of the stationary phase from the column leads to a reduction in the efficiency of separation and it also produces drift and "noise" in the zero line of the detector. The carrier gas entering the column should be carefully dried to avoid hydrolysis of the polyesters [30,67]. If the column is well stabilised and correctly operated, it should last for several months [23].

(*b*) Properties of polar liquid phases. Intermolecular attraction arises between the polarisable double bonds of unsaturated fatty acids and the ester groups of the polar liquid phases, and this increases with the number of double bonds in the aliphatic chain. This attraction specifically retards unsaturated methyl esters on the chromatogram, and they are found after the corresponding saturated esters, *i.e.* in the reverse order to that observed in chromatography on non-polar liquid phases [23].

Because of the weakening of London dispersion forces on polyester columns, the retention volume of the methyl esters of saturated acids, for the same temperature and weight content of liquid phase, is lower by a factor of 2–3 compared with columns of Apiezon L, and the chromatographic separation is correspondingly accelerated [15]. The free energy of solvation per CH_2 group is also reduced, and the separation factor of esters differing by a CH_2 group becomes smaller than on a non-polar column (1.40 instead of 1.56) [23]. Esters of branched-chain saturated acids, the distribution of which is governed by London forces, are found in front of the corresponding straight-chain saturated esters, as with non-polar phases [33,87]. The arrangement of double bonds in the chain and their geometric configuration have much less influence on V_R than when non-polar liquid phases are used [23].

The solubility of methyl esters of unsaturated fatty acids increases in *all* polar liquids as the number of double bonds in the chain increases. For this reason, mono-, di-, and tri-unsaturated esters emerge from the column (in that order) immediately after the saturated esters containing the same number of carbon atoms. At the same time, differences in the polarity of polyesters of differing composition considerably influences the effectiveness of the separation.

If the number of carbon atoms in the dibasic acid residue linked to the polyethylene glycol is reduced, or the monobasic acid residue in acylated β-cyclodextrins is shortened, the polarity of the polyester and the separating power of the column are increased; the thermal stability of the liquid phase and the absolute retention volume of methyl esters are reduced [14,86]. Methyl oleate can be completely separated from methyl stearate on columns with poly(ethylene glycol succinate), and they can be partly separated on columns with poly(ethylene glycol adipate) [12,24,30,51]. On strongly polar phases the relative retention of unsaturated esters increases to such a degree that the peak of the triunsaturated methyl ester overlaps the peak of the saturated ester containing two more carbon atoms. Thus on columns containing poly(ethylene glycol succinate) or poly(ethylene

‡ A second polymethylene chain should presumably have been included at one end of this unit (Ed. of Translation).

glycol pentaerythritol adipate) (LAC-2-R446) the ratio of the retention volume of methyl linolenate to that of methyl arachidate is unity; this ratio becomes greater than unity when the polarity of the column is increased, with an increased amount of liquid phase and a higher working temperature. Pairs of methyl esters of this kind are usually separated on less polar polyester phases such as poly(ethylene glycol adipate), poly(butanediol succinate), and poly(diethylene glycol sebacate)[24,30,51,88].

When a polyester column is kept at a high temperature for several weeks, the polarity of the phase is reduced[15]; this suggests the possibility of using columns that have been heated in this way to separate pairs of methyl esters that cannot be separated on "fresh" columns of the same polyester[33].

(*c*) Separation on polar liquid phases. Polyester phases have given the best results in the analysis of methyl esters of animal and vegetable fatty acids differing in chain length from C_1 to C_{30} and having 1–6 double bonds[14].

Nine branched-chain methyl, dimethyl, and trimethyl isomers of methyl heptadecanoate have been separated on columns of β-cyclodextrin valerate, butyrate, propionate, and acetate[86].

Unsaturated esters with the same number of carbon atoms and double bonds but differing in the positions of the bonds in the chain were difficult to separate on a packed column, though they could be separated on capillary columns. The 8,11-, 9,12-, 10,13-, and 11,14-isomers of methyl linoleate were completely separated on a capillary column of poly(ethylene glycol glutarate) from one another and from the methyl esters of stearic, oleic, and linolenic acids; on an ordinary column of poly(ethylene glycol adipate) only the 11,14-isomer and the 8,11- + 9,12-isomers were separated V_R slightly increased as the distance from the double bond to the carboxyl increased, but the methyl esters of oleic and petroselinic acids could not be separated on either column[73]. The methyl esters of linolenic and linoleic acids with conjugated double bonds were well separated from the corresponding esters with isolated bonds[34].

The *cis*- and *trans*-isomers of unsaturated acids are not separated[12,63] on a packed column. Methyl oleate has been separated from methyl elaidate, which had a lower V_R, on a capillary column of poly(ethylene glycol succinate). The geometric isomers of methyl linoleate have been separated into *trans*-*trans*, *cis*-*cis* + *cis*-*trans*, and *trans*-*cis* forms, and the isomers of methyl linolenate into *trans*-*trans*-*trans*, mono-*trans*, di-*trans*, *cis*-*cis*-*cis* + + di-*trans*, and mono-*trans* + mono-*cis* forms. The separation of geometric isomers of methyl linoleate with conjugated double bonds was as effective as on a non-polar column[25].

The chromatography on a polyester column of methyl *cis*-9,10-epoxyoctadecanoate and its derivatives has been described[46]. Methyl *erythro*- and *threo*-dibromooctadecanoates have been separated on a succinate polyester column; the *threo*-form with the larger dipole moment was found to have the higher retention volume. V_R for the *threo*-form was 20 times the value of V_R for methyl stearate[64].

7. Identification of Fatty Acids

Methods of identifying fatty acids in complex natural mixtures may be divided into two main groups — (*a*) identification from chromatographic results obtained under different conditions, varying with respect to polarity of the liquid phase, composition of the solid carrier, type of detector, separation temperature, speed of gas, etc.; and (*b*) identification by a combination of chromatographic and non-chromatographic methods (oxidative cleavage, halogenation or catalytic hydrogenation of double bonds, ultraviolet and infrared spectrophotometry, mass spectrometry, etc.).

(*a*) Gas-chromatographic identification. The retention volumes V_R of the methyl esters of fatty acids vary considerably with the parameters of the experiment; for identification purposes the separate components of a mixture are usually characterised by the relative retention volume V_R^{rel}, which is equal to the ratio of V_R for the given ester to V_R for a known compound (methyl ester of myristic, palmitic, or stearic acid[51]). V_R is measured from the centre of the air peak[28]. The simplest method of chromatographic identification is that based on the value of V_R^{rel}; however, because two or more components may be contained in one chromatographic band, this method of identification is not always reliable in the analysis of complex mixtures of fatty acids[14]. Identification of branched-chain and unsaturated acids from the separation factor has been described in Section II, 3.

Like other processes of partition chromatography, the gas-chromatographic separation of lipids follows an additive rule[58,60-86]. According to this rule, the addition of a new functional grouping changes the partition coefficient by an amount depending only on the nature of this grouping and its distribution between the phases of the chromatographic system, but independent of the composition of the remainder of the molecule. On non-polar and polar phases the values of $\log V_R^{rel}$ when plotted against the number of carbon atoms in a homogeneous series m give a family of parallel lines. This holds for the methyl esters of normal saturated fatty acids[51], branched-chain saturated acids, iso and (+)-anteiso branched-chain acids[87], monounsaturated acids[51,87], di-, tri-, and poly-unsaturated acids[23], brominated fatty acids[64], mono- and di-basic short-chain acids[77], etc.; it holds also for hydrocarbons[90], aliphatic aldehydes[91], triglycerides[92], and other lipoids. For methyl esters of the same chain length a linear relation between $\log V_R^{rel}$ and the number of double bonds has been established[51]. The functional dependence for saturated acids is described by an equation of the type $\log V_R^{rel} = a + bm$, where a and b are constants depending on the experimental parameters[19,21]. As the separation temperature rises, the slopes of the parallel lines decrease[93]. Fatty acids can be identified from the linear dependence of $\log V_R^{rel}$ on m, if the homologous series to which they belong is known.

If the homologous series is not known, the methyl ester is identified from the value of V_R^{rel} on columns with non-polar and polar liquid phases by means of a relationship observed by James for straight-chain saturated and unsaturated acids with isolated double bonds. He showed that there is a linear dependence between values of $\log V_R^{rel}$ for the methyl esters of a given homologous series on columns with Apiezon L and poly(ethylene glycol adipate); saturated and mono-, di-, tri-, and poly-unsaturated fatty acids form a series of parallel lines. The point of intersection of the value of $\log V_R^{rel}$ with one of these lines enables an unknown acid to be characterised with respect to the number of carbon atoms and the number of double bonds. The points of intersection corresponding to esters of the same chain length but differing in unsaturation lie along the perpen-

dicular drawn to the straight line for esters of saturated acids at the point corresponding to the methyl ester of the saturated acid with the given number of carbon atoms [23]. Similar relationships have been obtained for the separation of mixtures of fatty acids on two polyester columns differing in polarity [86].

The value of V_R^{rel} may be expressed for identification purposes by the number of carbon atoms in the saturated fatty acid; this quantity has been termed the "carbon number" [75] or the "equivalent chain length" (ECL) [94]. To calculate the ECL of an unidentified chromatogram peak, a reference line is drawn for the dependence of $\log V_R^{rel}$ of methyl esters of normal saturated fatty acids on the number of carbon atoms m for the given separation conditions, and from this line the value of m corresponding to the value of $\log V_R^{rel}$ for the component to be identified is read; the value of m obtained is the ECL of the methyl ester. In the absence of a reference line the ECL can be calculated from the equation

$$\mathrm{ECL} = (s_2 - s_1)\frac{\log(t_x : t_{s_1})}{\log(t_{s_2} : t_{s_1})} + s_1,$$

where s_1 and s_2 are the ECL's of the standard methyl esters and t_x, t_{s_1}, and t_{s_2} are the V_R^{rel} values for the ester under investigation and the standards [93]. Obviously, for saturated esters the values of ECL on polar and non-polar phases coincide and are equal to the number of carbon atoms in the aliphatic chain. The inclusion of a double bond or a certain functional group in the molecule gives a known increment to the ECL compared with that of the saturated ester having the same chain. Table 3 shows the increments in the ECL for several substituents.

When the ECL of an unknown component has been determined on columns with polar and non-polar liquid phases, the component and its functional groups may be identified. ECL values have been used to identify nine isomers of branched C_{17} fatty acids on polar phases consisting of acylated β-cyclodextrins [95].

Recently methods have been developed that permit not only the number but also the positions of isolated double bonds in a fatty acid chain to be determined from V_R^{rel} values obtained with highly polar liquid phases [96-98]. When the double bonds are displaced from the central position towards the carboxyl or methyl end of the aliphatic chain, V_R^{rel} on polyester phases increases in such a way that, when values of $\log V_R^{rel}$ for the methyl esters of the unsaturated acids are plotted against the number of carbon atoms, parallel lines between the points corresponding to fatty acids having the same number of unconjugated double bonds can be drawn only if these acids contain the same number of carbon atoms between the centre of the double bond most remote from the carboxyl and the terminal methyl group inclusive, *i.e.* when the increase in methylene groups in the homologous series occurs only at the carboxyl end of the chain [96]. Similar series of parallel straight lines have been obtained by grouping unsaturated fatty acids with the same number of carbon atoms between the carboxyl and the centre of the nearest double bond, and also acids with the same degree of unsaturation and an equal number of carbon atoms, in which the double bonds are regularly displaced from the carboxyl end of the aliphatic chain to the methyl [97]. The structure of the polyunsaturated acids of whale oil has been determined by using these graphs to compare experimental values of $\log V_R^{rel}$ with values for esters having a known arrangement of double bonds [98].

TABLE 3. Increments of equivalent chain length for various functional groups in the gas–liquid chromatography of methyl esters of fatty acids on non-polar and polar liquid phases.

Substituent	Apiezon	Poly(ethylene glycol adipate)	Ref.
cis-9,10-Double bond	−0.3	+0.4	94
cis-9,10-12,13- Double bonds	−0.4	+1.0	93
trans-9,10-11,12-Conjugated double bonds	+0.7	+2.6	94
Cyclopropene ring	−0.4	+1.0	93
$COOCH_3$ group	+2.6	+7.3	94
9-CH_3 group	−0.7	−0.8	93
4-CO group	+1.3	+1.8	93
9-CO group	+1.4	+5.7	93
12-OH group	+1.7	+6.3	94
9,10-$(OH)_2$ group	+3.3	+11.8	94
cis-9,10-Epoxy-group	+2.0 *	+4.0 **	46

* Chromatography on a silicone column.

** Chromatography on a column of poly(butane-1,4-diol succinate).

(*b*) Combination of chromatography with non-chromatographic methods. Esters of fatty acids with the same number of carbon atoms and the same number of double bonds in different positions on the chain cannot be separated on non-polar liquid phases; the separation of such esters is also sometimes impossible on polyester phases (methyl oleate and methyl petroselinate). To identify unsaturated acids in such cases, they are oxidised at the double bonds and the products are determined by gas chromatography.

Oleic, linoleic, and other fatty acids were oxidised with $KMnO_4$ in acetic acid at -70°, the excess of permanganate was destroyed with metabisulphite, and methyl esters of the di- and mono-basic acids obtained were separated on a column with Apiezon M. Azelaic and pelargonic acids were found among the oxidation products of oleic acid. The presence of numerous by-products of the oxidation shows that in this case the unsaturated acid chain was broken not only at the double bonds but also at other positions [77]. This method has been used also for the identification of unsaturated acids from fish oils [69]. Oxidation with a $KMnO_4$–KIO_4 mixture also gave many secondary degradation products [99]. No oxidation by-products were produced when unsaturated acids were oxidised with performic acid, the unsaturated dihydroxy-acids obtained were hydrogenated over a palladium catalyst, and the dihydroxy-grouping was ruptured with $KMnO_4$–KIO_4 mixture to give all possible mono- and di-basic acids. Fatty acids containing triple bonds underwent hardly any degradation in this series of reactions [100].

The chains of unsaturated acids may be ruptured by either oxidative or reductive ozonolysis. In the first case the fatty acids are ozonised in chloroform solution at -60°, and the ozonide is decomposed by water with simultaneous oxidation of the terminal carbon atoms to carboxyl under the action of Ag_2O. The acids obtained are converted into methyl esters, and separated by gas–liquid chromatography using programmed temperature conditions [101,102]. Oxidative ozonolysis of the decomposition products of polyunsaturated fatty acids containing non-conjugated double bonds has made possible the isolation of malonic acid, which is formed on elimination of a $-CHCH_2CH-$ group: periodate oxidation destroys malonic acid [103].

The most reliable information on the structure of unsaturated acids is obtained by reductive ozonolysis. The ozonides formed at low temperatures are decomposed with H_2 in the presence of a palladium catalyst or by reduction with triphenylphosphine; aldehyde groups are formed at the positions where double bonds have been broken. Gas chromatography of the aldehydes and dialdehydes is carried on an apparatus with a flame-ionisation detector, since malonaldehyde is difficult to observe with an ionisation detector [61,68,104].

Infrared spectroscopy (detection of *trans*-isomers) [33], mass spectrometry [105], and also a combination of gas–liquid chromatography with other types of chromatography [33,76]. have been used to identify acids after separation.

8. Quantitative Determination of Fatty Acids

Gas–liquid chromatography enables a quantitative determination of saturated and unsaturated fatty acids to be carried out with much greater speed and precision than any other method in lipid chemistry. For a quantitative analysis the signal of the detector must be directly proportional to the weight concentration of the given methyl ester, and also of methyl esters of fatty acids with different structures [10]. The relative area of the corresponding peak in the differential chromatogram usually serves as a measure of the quantity of a component in gas chromatography. There are a number of methods for measuring the areas of peaks — (1) weighing the paper, (2) planimetry, (3) calculation of the product of the height of the peak and its width at half its height, (4) calculation of the product of peak height and retention volume, and (5) continuous determination during chromatography by means of an integrator. Although method (3) is the most widely used [59] because of its simplicity and reliability, for speed and accuracy integration is superior to all other methods [106].

In their first paper on gas–liquid chromatography, James and Martin determined free fatty acids by using a titration cell with alkali solution containing an acid–base indicator; change in colour of the indicator when it absorbed volatile fatty acids from the column was measured by a colorimeter connected to a potentiometer that recorded an integral curve. The height of each step corresponded to the molar content of the given fatty acid [1].

Later the same workers used as detector a Martin balance to measure the density of the gas, which enabled the sample size to be reduced [58]. The balance gives figures directly proportional to the mass of the organic compound being separated, and therefore does not require calibration for different methyl esters; until recently, however, Martin balances have not been much used because of their complex construction [22,28,54].

Satisfactory results have been obtained by using a flame-ionisation detector, where the signal depends linearly on the concentration of fatty acids in the mixture [107]. Nevertheless, the katharometer and the Lovelock ionisation detector are most widely used; we shall consider their operation in detail.

(*a*) Katharometer. A katharometer, measuring the difference between the thermal conductivity of an inorganic carrier gas and that of an organic compound, was first used for the gas-chromatographic analysis of methyl esters of higher fatty acids in 1953 [18]. The sensitivity of the katharometer is $\sim 10^{-6}$ g. At higher separation temperatures the detector becomes less sensitive, so that the volume of the sample must be increased [15]. To determine the absolute amount of fatty acids, an internal standard is used in the sample. Before the analysis an aliquot of methyl heptadecanoate is added to a known volume of sample — this compound does not usually occur in biological material — and the ratio of the areas of the peaks of methyl esters to that of the standard is calculated [35,36,51].

In the fatty acid series a linear relation has been observed between the logarithm of the peak area and the logarithm of the corresponding weight [37]. Comparative quantitative determinations have been made of the composition of fatty acids by chromatography with a katharometer, and also by standard non-chromatographic methods [108,109]. It was found that on polyester liquid phases the katharometer gave high results in measurements on the more volatile saturated components, but for esters with a high retention volume the results were low [30,110,111]. An explanation suggested for this phenomenon was that more intense transesterification occurs between the high-boiling components and the column polyesters at a high separation temperature: in fact, when the temperature of the column was reduced to 200°, the difference in the results obtained by different methods was greatly reduced [51]. However, the same effect was later observed in chromatography on a non-polar liquid phase (Apiezon), where the possibility of transesterification was excluded [112,113]. Other workers have explained the differences by imprecise measurement of the peak areas with large retention volumes [24].

Detailed investigation of standard mixtures of methyl esters of known composition has shown that in the fatty acid homologous series the specific thermal conductivity is not proportional to molecular weight. Thus if the area of the peak relating to 1 mg of compound is taken as 1.00 for methyl decanoate, the area for methyl stearate is only 0.84. [112] The following empirical equations have been proposed to correct the thermal conductivity: $\log A = m \log M + \log K$, where A is the peak area, M the weight of compound, m the number of carbon atoms, and K a constant [114]; $R = 24.68 + 5.79m + 0.075m^2$, where R is the relative molar signal of the detector based on the signal for methyl palmitate [115]; $\log y = 0.001007x - 0.161$, where y is a correction factor and x the relative retention volume [116]. Kaufmann has observed a linear dependence between the calibration factor (ratio of weight content of methyl ester to peak area) and the number of carbon atoms in a given homologous series of fatty acids [106].

All these investigations have shown that precise quantitative results can be obtained in work with a katharometer only after the detector has been carefully calibrated with standard mixtures of methyl esters for the given conditions of sample size, current in sensitive cell, rate of flow of carrier gas, and temperature and nature of column [35,48]; after the same column has been working for some time the calibration is repeated, or corrections corresponding to new values of V_R are determined from a graph [116]. A Martin balance may be used as standard in calibrating the detector [11].

(*b*) Ionisation detector. In 1958 Lovelock [117] proposed a new type of detector, in which the organic compounds are detected and quantitatively determined by ionisation with metastable argon atoms produced by the action

of ionising radiation. The following reactions occur in the detector:

$$Ar + \beta \text{ particles} \rightarrow Ar^+ + e^-, \quad (1)$$

$$Ar + e^- \xrightarrow{\text{high voltage}} Ar^* \ (11.6 \text{ eV}), \quad (2)$$

$$\text{Organic compound} + Ar^* \rightarrow \text{organic compound}^+ + e^- + Ar, \quad (3)$$

$$e^- \xrightarrow{\text{to anode}} \text{ionisation current}. \quad (4)$$

When argon passing through the detector is irradiated with β particles from ^{90}Sr, metastable argon atoms with an excitation potential (11.6 eV) which is above the ionisation potentials of most organic compounds are formed in addition to argon ions. Ionisation of organic compounds leads to an increase in the ionisation current, which is registered on a recording potentiometer. The high sensitivity of the ionisation detector (10^{-9} g) enables it to be used for the separation of small quantities of material, which greatly increases the effectiveness of the column. For esters with a molecular weight of 150 and higher, the peak area corresponds to the weight content of a given methyl ester in the mixture; therefore the detector does not require calibration[12,35,118].

The linear dependence of the detector signal on the concentration of a compound in the stream has been confirmed within certain limits in the analysis of standard mixtures of methyl esters of higher fatty acids[63,119,120]. The relative error in measuring the concentration of the maximum peak did not exceed 1%.[35] As a check on the linearity of the signal, free C_4–C_{10} fatty acids were separated on a non-polar column with Apiezon L: if the carboxyl occupied a large volume in the acid molecule, the signal on the ionisation detector was somewhat less than that corresponding to the weight content of the component[113]. The peak areas of the lower fatty acids are proportional to their mole percentages[118]. An appreciable deviation has repeatedly been observed in the analysis of samples containing methyl linolenate[60]. Thus, the linolenic acid content of linseed oil was found to be 46.4% by ultraviolet spectrophotometry and 54.2% by gas chromatography with an ionisation detector[50]. The reason for this behaviour of linolenic acid is still obscure.

Notwithstanding the complications mentioned above, its high sensitivity, simplicity, and reliability make the ionisation detector superior to other types of detector. At present this detector is used more often than others in the quantitative determination of methyl esters of higher fatty acids.

9. Determination of Radioactivity of Fatty Acids with Gas-Chromatographic Separation

In biological investigations in which labelled atoms are used it is necessary to determine the separate compounds qualitatively and quantitatively and in addition their radioactivity must be measured. A number of methods have been proposed for solving this problem in gas–liquid chromatography. The methods may be divided into two groups: in the first group the separate fractions emerging from the column are preparatively trapped and their radioactivity is determined after their chromatography has been completed; in the second group the mass and the radioactivity of the fractions are measured simultaneously at the outlet of the column while the separation is in progress.

Traps for the preparative collection of fractions may consist of short glass tubes filled with anthracene crystals coated with silicone oil[70,121], tubes containing cotton wool moistered with toluene and kept at room temperature[132], collectors with a cooling gradient[123], spiral condensers with glass powder on the inner walls[69], or special microporous filters[124]. With an ionisation detector there is practically no degradation of the sample in the detector; samples of methyl esters emerging from the column can therefore be collected without loss[117]. As the fractions are collected the traps are changed by hand[121,122] or by means of an automatic fraction collector[70]. The methyl esters collected are eluted with a solution of scintillators (2,5-diphenyloxazole and 2-*p*-fluorophenyl-5-phenyloxazole) in toluene, and measurements are made to the required accuracy on a scintillation spectrophotometer. Usually ~90% of the radioactivity introduced into the column is trapped[122]; the remainder of the activity emerges from the column later because it is held up by transesterification of the methyl esters with the polyester liquid phase and their adsorption on the solid carrier[65,72]. This delay can be reduced if the carrier is treated before addition of the liquid phase with hydrochloric acid and alkali, the transesterification catalyst (toluene-*p*-sulphonic acid) is removed from the liquid phase, and the separation is carried out at the lowest possible temperature[65,70,72]. The method of collecting fractions is used in work with samples having low radioactivity.

If the activity of the separate methyl esters exceeds a count of 1000 min^{-1}, more rapid methods in which radioactivity is continuously recorded should be used[125]. The vapours emerging from the column condense in a cooled solution of scintillator circulating very rapidly under the action of a gas stream in a closed system of tubes between windows of one or two spectrometer photomultipliers. The radioactivity of the solution is recorded as an integral curve, the height of a separate step being proportional to the activity of a given methyl ester; this curve is combined in due course with a differential curve recording the mass, the peaks are identified, and the specific radioactivity of each ester is determined. The efficacy of counting on such an apparatus reaches 80% for ^{14}C and 28% for ^{3}H.[126,127] If the retention volumes of adjacent components on the differential chromatogram are close (methyl stearate and methyl oleate), the esters cannot be separately determined on an integral radioactivity curve[70].

In another method lipids at the outlet from the column are burned over CuO to CO_2 and water; the water is absorbed by activated $MgClO_4$ or reduced to hydrogen, and the activity of the $^{14}CO_2$ is determined on a proportional or scintillation counter, a differential radioactivity curve being recorded[128,129].

III. GAS–LIQUID CHROMATOGRAPHY OF FREE FATTY ACIDS AND THEIR DERIVATIVES (OTHER THAN METHYL ESTERS)

1. Separation of Free Fatty Acids

Gas–liquid partition chromatography was proposed in 1952 by James and Martin as a method for separating volatile C_1–C_{12} free normal aliphatic acids[1]. A column of kieselguhr impregnated with a mixture (9 : 1) of silicone oil and stearic acid was used; this acid was included in the liquid phase to suppress dimerisation of the aliphatic acids, the molecules of which are highly polar. The association of carboxyls and the formation of dimers, which lowers the

volatility of the acids and leads to the formation of unsymmetrical diffuse zones on the chromatogram, may also be reduced somewhat by changing the amount of test sample and the concentration of liquid phase on the column, as well as the working temperature[6]. At present separation in the free form is confined almost entirely to the lower aliphatic acids[14,130]. Only a few papers have been devoted to the gas chromatography of the free higher fatty acids. The conditions for separating these acids are given in Table 4.

As Table 4 shows, dimerisation of free acids has been suppressed by the use of polar liquid phases containing a non-volatile mineral acid[82,131]. Free fatty acids in low concentrations have been separated on a column with a non-polar phase, when an increase in working temperature reduced the asymmetry of the peaks[22]. On a polyester column the asymmetry of the peaks increased with rise in temperature and also as the concentration of the liquid phase was lowered[132]. Under all separation conditions considerable stretching of the rear of the peak ("tailing") was observed.

In comparison with the corresponding methyl esters, the free acids exhibit higher retention volumes V_R^{20}; the separation of saturated and monounsaturated fatty acids was less sharp, and quantitative determination with a katharometer was difficult, because of differences in thermal conductivity between the acids and the methyl esters[82,132].

2. Separation of Hydrocarbons, Alcohols, Aldehydes, and Amines

Higher hydrocarbons present in many vegetable and animal products are usually extracted by adsorption from the remaining lipoids as the least polar fraction, and are separated without further treatment on a column with a non-polar liquid phase at 270–300°;[133,134] no difference in V_R is observed between saturated and unsaturated hydrocarbons of the same chain length[135]. Hydrocarbons are much more volatile than alcohols: V_R for hydrocarbons with an even number of carbon atoms C_{2m} corresponds with V_R for the primary aliphatic alcohols having four fewer carbon atoms C_{2m-4}.[90] Usually organisms contain the normal C_{16}–C_{34} hydrocarbons with a preponderance of either even or odd components[133,136]. Sometimes alcohols or methyl esters of acids are reduced to hydrocarbons, and the latter are determined by gas–liquid chromatography[134,135].

Free aliphatic alcohols can be separated on a column with a liquid phase[136,137], but alcohols with different degrees of unsaturation are not separated from one another[135]. Free alcohols are poorly separated on columns with polar polyesters, because of transesterification with material of the liquid phase[138]: acetates of unsaturated and saturated C_5–C_{18} aliphatic alcohols have been separated well on polyester phases[139]. When the temperature of the column is raised to 180°, compounds with the same number of carbon atoms and one ester bond are separated, for example the methyl ester of a monobasic acid and the acetate of the primary alcohol, such as methyl laurate and undecyl acetate; this separation is impossible at 130°.[140]

Aliphatic aldehydes from brain plasmalogens form dimethylacetals on methanolysis in the presence of HCl, and these can be separated on columns with polar or non-polar liquid phases[91,138].

When chromatographed with non-polar liquid phases, aliphatic amines react with the material of the column; the reaction ceases when the solid carrier has been washed with methanolic KOH.[141]

3. Separation of Glycerides

Because of their high molecular weights, mono-, di-, and particularly tri-glycerides are only slightly volatile, and the gas–liquid chromatography of these compounds is therefore still at the stage of preliminary experiments. Conditions for the separation of triglycerides are given in Table 5. This shows that at the high temperatures required for the analysis of triglycerides only non-polar silicone liquid phases may be used. These phases separate triglycerides only according to the number of carbon atoms in the molecule; there is no separation based on unsaturation. Polyester phases cannot be used here because of their low thermal stability.

Satisfactory gas-chromatographic separation of triglycerides would provide the most direct and shortest path to a study of the composition and structure of these lipoids; for this reason, several attempts have been made in this direction. Initially, separation of the lipoids of butter-fat and coconut oil was achieved only as far as trimyristin C_{42}, and numerous decomposition products were obtained[142]; then the glycerides of palm-kernel oil and lard were separated as far as C_{52}.[143] Recently fractions of C_{28}–C_{60} triglycerides differing by two carbon atoms have been separated from various seed oils and butter-fat, as well as triglycerides of odd and branched fatty acids. There is no contamination with thermal decomposition products at the beginning of the chromatogram[92]. This method has been used on triglyceride fractions obtained by molecular distillation[144].

For gas chromatography mono- and di-glycerides must be converted into volatile derivatives, for example acetates. Monoglycerides up to monoarachin and diglycerides up to palmitomyristin have been separated as acetates; the acetates of 1-mono- and 1,3-di-glycerides are eluted

TABLE 4. Gas–liquid chromatography of free higher fatty acids.

Solid carrier	Liquid phase and its content	Temp., °C	Carrier gas	Gas flow, ml min^{-1}	Detector	Composition of sample and duration of analysis, min	Ref.
Celite 545, 50–100 mesh	Apiezon L, 20%	300	N_2	12	katharometer	C_{14}–C_{22}, 90	22
Celite 545 60–80 mesh	poly(ethylene glycol adipate), 25% + H_3PO_4, 2%	220–235	He	30–40	katharometer	C_8–C_{20}, 60–80	131
Kieselguhr	Reoplex-400, 5–20%	165	Ar	35–50	ionisation	C_4–C_{18}, 90	132
Glass beads 0.75–1.00 mm	poly(ethylene glycol succinate), 1% + + H_3PO_4, 0.4%	140–200	Ar	60	ionisation	C_6–C_{18}, 40	82

TABLE 5. Gas–liquid chromatography of triglycerides.

Solid carrier	Liquid phase and its content	Temp., °C	Carrier gas	Gas flow, ml × × min^{-1}	Detector	Composition of sample and duration of analysis, min	Ref.
Chromosorb W	silicone, 30%	347	He	200	katharometer	C_{30}–C_{42}, 90	142
Ditto	silicone rubber, 2%	programmed, 100–360	He	145	»	C_{18}–C_{52}, 25	143
»	methylsilicone rubber, 2.25%	ditto, 220–325	N_2	150	flame-ionisation	C_{30}–C_{60}, 30–50	92

more rapidly than the derivatives of 2-mono- and 1,2-di--glycerides respectively[145]. To determine 1- and 2-monoglycerides, a mixture of them is treated with methanesulphonyl chloride, and then with a solution of sodium iodide in acetone; the allyl esters of the fatty acids obtained are separated on a column with a non-polar liquid phase at 240° in 60 min. In NaI solution the acid residue of the 2-monoglyceride migrates to the extreme position; 1- and 2-monoglycerides therefore give products of the same composition. The fatty acids of 2-monoglycerides are determined after removal of the 1-monoglycerides by periodate oxidation[146]. This method might be useful in studying the specific hydrolysis of triglycerides by pancreatic lipase[6].

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In recent years there has been a continuous and ever increasing growth of gas-chromatographic methods in both theoretical and practical directions, and also in the wider application of this type of chromatography to the study of the most diverse problems in the chemistry and biochemistry of fatty acids and lipids.

Nevertheless, gas chromatography is still not a universal means of solving any problems that the development of science might present to the research worker. Like any other method, it has definite limitations, and it is only by skilfully combining gas chromatography with thin-layer, partition, and other types of chromatography, as well as with non-chromatographic methods — molecular and nuclear spectroscopy, mass spectrometry, X-ray analysis, specific enzyme hydrolysis, radioisotope methods, etc. — that we can hope to overcome successfully all the difficulties associated with the study of the chemical structure of plant, animal, and microorganism lipids and with the study of the part played by lipids in metabolism.

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OSCILLOGRAPHIC POLAROGRAPHY IN ORGANIC CHEMISTRY

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I. INTRODUCTION

The method of oscillographic polarography is based on the interpretation of curves obtained during the electrolysis of test solutions and recorded by a cathode-ray oscillograph. In ordinary or classical polarography the voltage applied to the polarographic electrolysis cell is varied according to a linear law, the rate of change of potential of the polarised electrode being deliberately selected at a low value of about 5 mV s^{-1} so that it has no influence on the shape of the polarogram. In oscillographic polarography the rates of change of potential vary from several millivolts to tens of volts per second. In some cases the rate of change of potential of the polarised electrode may reach several hundred volts per second. With a comparatively high rate of change of potential the current also changes rapidly, and a cathode-ray oscillograph is therefore used to measure the current; hence the name oscillographic polarography.

The methods of oscillographic polarography can be divided into two groups, depending on the form of the voltage applied to the polarographic cell. In the first group of methods, the voltage applied to the cell increases linearly. In the second group, it increases non-linearly, in particular sinusoidally.

The first papers on oscillographic polarography appeared about twenty years ago [1,2] and described chiefly the design and use of the instruments. Later, oscillographic polarography began to be employed as a highly sensitive analytical method. The most widely used methods have been those in which current–potential ($i-E$) curves are recorded with a voltage of triangular form applied to the cell, or in which curves for rate of change of potential as a function of potential, $dE/dt = f(E)$, are recorded with an applied voltage of sinusoidal form.

The general principles of oscillographic polarography and the theory of the method have been described in detail in a number of monographs [3-6] and reviews [7-12]. Oscillographic polarography is one of the newest instrumental methods of study, and is finding extensive application primarily in analytical chemistry. The value of the method is not restricted to analytical problems, however. Oscillographic polarography is widely used in organic chemistry, pharmacology [13-17], biochemistry [18,19], medicine [20,21], and oceanography [22]. In the present review an attempt is made to show how oscillographic polarography can be used to solve problems in theoretical organic chemistry. We shall deal chiefly with oscillographic polarography using alternating current, which gives $dE/dt = f(E)$ curves. This method is now the most fully developed with regard to both theory and apparatus. For comparison and comparative characterisation we shall give data from some work in which $i = f(E)$ curves were recorded.

II. PHYSICOCHEMICAL STUDIES BY OSCILLOGRAPHIC POLAROGRAPHY

For the sake of brevity we shall refer to the methods of oscillographic polarography in which the dependence of dE/dt on E and the dependence of i on E are recorded as the dE/dt method and the $i-E$ method respectively.

The polarisable electrodes used in oscillographic polarography are the same as those used in classical polarography, *i.e.* the dropping mercury electrode, the hanging mercury drop [23-25], and solid electrodes [26]. In addition, jet electrodes are widely used in oscillographic polarography. Calomel electrodes, carbon electrodes, and the mercury macroelectrode are usually employed as reference electrodes.

To obtain oscillographic curves by the dE/dt method, an alternating current of about 0.5 mA with the dropping electrode and 5 mA with the jet electrode is passed through the polarographic cell. The mains are generally used as source of a.c. of frequency 50 c/s. [27]

In the absence of an electrochemically active substance, the $dE/dt = f(E)$ curve on an alkaline supporting electrolyte has an oval shape (Fig. 1). In the presence of a depolariser, the curve shows the appearance of incisions whose depth depends on the concentration of the depolariser and whose position along the potential axis depends on the nature of the depolariser.

The oscillogram for a solution containing a depolariser (Fig. 1) has two branches. The upper branch corresponds to the cathodic process and the lower branch to the anodic process. The extreme left-hand point of the curve corresponds to the dissolution potential of the mercury electrode, and the extreme right-hand point to the reduction potential of the cation of the base electrolyte.

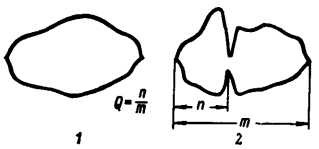


Fig.1. Oscillopolarographic $dE/dt = f(E)$ curves for:
1) 0.2 M NaOH solution;
2) 3×10^{-4} M benzil in the same solution.

Since several polarisation cycles take place during the lifetime of a single drop, a family of oscillograms can be obtained on the oscillograph screen for each drop. Therefore if a dropping mercury electrode is used, the oscillogram for the test solution is recorded in the last period of existence of the drop, when its surface is changing only slowly.

The theory of oscillographic polarography with a.c. is based on the general integral equation describing processes at a mercury electrode with polarisation by a current which changes as some function of time. Exact solution of this equation is possible only if we make certain assumptions, which are not, however, always experimentally justified. Kambara[28] and Madsuda[29] were the first to derive an equation for the oscillographic curve, but they made no allowance for the charging current in their calculations.

The form of the $dE/dt = f(E)$ curve was calculated approximately by Micka[30,31] for reversible processes, most of the factors determining the electrochemical process being taken into account.

The differential of the potential with respect to time in the potential range where neither dissolution of mercury (the extreme left-hand point on the $dE/dt = f(E)$ curve in Fig. 1) nor reduction of the cation of the base electrolyte (extreme right-hand point on the same curve) is reached is given by the expression

$$-\frac{dE}{dt} = \frac{i_0 \sqrt{\omega} \cos\alpha}{\frac{n_1^2 F^2 P_1}{RT(1+P_1)^2}(\sqrt{D_1}C_{1a} + \sqrt{D_2}C_{2a}) + C'\sqrt{\omega}}, \qquad (1)$$

where i_0 is the current density per square centimetre of the electrode surface, ω the angular velocity, $\alpha = \omega t$ + const = = the phase angle, n_1 the number of electrons taking part in the reduction of the substance, C' the specific differential capacity, D_1 and D_2 are the diffusion coefficients of reduced and oxidised forms of the depolariser, C_{1a} and C_{2a} the corresponding concentrations, R and T the usual thermodynamic constants, and P_1 is an exponential function:

$$\left(P_1 = \exp\frac{n_1 F}{RT}(E - E_1^{1/2})\right).$$

If we assume that the solution contains the depolariser exclusively in the oxidised form, *i.e.* that $C_{2a} = 0$, we find that the differential has a minimum value at the apex of the cathodic incision on the $dE/dt = f(E)$ curve. Calculations show that in the central potential range, from -0.5 to -1.5, where the incisions are most clearly defined, $\cos\alpha = 1$: *i.e.* the potential at the apex of the cathodic incision (and similarly the anodic incision) is equal to the half-wave potential of the depolariser.

The position of the incision on the potential axis is determined by the quantity Q, a quotient whose significance is apparent from Fig. 1. Other conditions being equal, the dimensionless quantity Q will naturally depend not only on the pH of the solution but also on the nature of the base electrolyte, since the latter determines the potentials at the extreme points on the curve. In the study of organic substances, Britton–Robinson buffer solutions and other buffer systems are usually employed. The potentials at the extreme points on the curve for these solutions (for a dropping mercury electrode) are found relative to a normal Weston cell and are used to determine the value of Q in volts. Table 1 gives potentials at the extreme points on the $dE/dt = f(E)$ curves for various buffer solutions.

An important feature is that the potential range in which the electrode is polarised is independent of the reference electrode used[8].

Close to the extreme points on the $dE/dt = f(E)$ curve, $\cos\alpha < 1$: *i.e.* the depth of the incision for a substance with a reduction potential which is either too positive or too negative is influenced by the steepness of the curve, which makes the incisions unsymmetrical and distorted with a reduced depth. In practice we usually deal with the relative depth h of the incision, which is equal to the ratio between the values of the derivative in the presence and in the absence of depolariser, and is defined as

$$h = \frac{KC}{KC + 4C'\sqrt{\omega}}, \qquad (2)$$

where C is the concentration of depolariser and $K = n^2F^2D^{\frac{1}{2}}/RT$.

From this it follows that the concentration dependence of the relative depth of the incision is hyperbolic, with one asymptote the horizontal axis. In practice this dependence is observed only approximately because of the various assumptions made in the calculation. Moreover, it follows from the formulae given above for the incision depth that the relative incision depth decreases only slightly with increase in the a.c. frequency, and this agrees with experiment.

In the absence of depolariser, *i.e.* when $C_{1a} = C_{2a} = 0$, the derivative is given by the expression

$$-\frac{dE}{dt} = \frac{i_0 \cos\alpha}{C'}, \qquad (3)$$

and for a given value of the current depends on the differential capacitance, which in turn depends on the electrode potential[32,33].

The dependence of differential capacitance on potential is characteristic of each electrolyte. Classical polarographic data can be used to estimate the magnitude of the

TABLE 1.

Polarographic support	E, V (s.c.e.)	
	left-hand point	right-hand point
1 M H_2SO_4	+0.41	−1.44
0.1 M HCl	+0.02	−1.47
Britton–Robinson buffers		
pH 1.81	+0.35	−1.50
pH 3.29	+0.29	−1.57
pH 4.10	+0.25	−1.61
pH 6.37	+0.18	−1.70
pH 7.96	+0.12	−1.75
pH 10.38	+0.07	−1.80
pH 11.98	+0.03	−1.84
0.1 M NH_4OH + 0.1 M NH_4Cl	−0.01	−1.92
0.1 M LiCl	+0.01	−2.20
0.2 M NaOH	−0.083	−1.96
0.2 M KOH	−0.080	−1.92

integral capacitance of the dropping mercury electrode[34]. For example, if the capacitance of such an electrode is 0.3 μF, the capacitive current for a rate of change of potential of 2 V s^{-1} is 6×10^{-7} A, which is no greater than the usual value in classical polarography. In the case of a.c. (*e.g.* 50 c/s), however, the rate of change of potential is large, and the capacitive current increases accordingly, reaching the same order of magnitude as the current produced by the electrochemical reaction. Thus oscillographic polarography makes it possible to study compounds which may not only react electrochemically at a polarisable electrode but also be adsorbed on its surface.

At a definite potential for each substance, an adsorption maximum is observed, reflected on the $dE/dt = f(E)$ curve by an incision of varying shape (sharp or in the form of an oval depression), often very similar to the depolariser incision. This phenomenon is observed in dilute electrolytes (*e.g.* 10^{-3} M sulphuric acid) and corresponds to the minimum in the differential capacitance of the mercury electrode at a definite potential. The nature of the incision can be determined by changing the a.c. frequency. If it is capacitive in character, its relative depth is insensitive to change in frequency.

Moreover, the depth of incisions due to capacitive phenomena decreases with increase in temperature, whereas the opposite relationship is observed for electrode processes involving electron transfer.

In order to determine whether the process recorded on the $dE/dt = f(E)$ curve is a capacitive process, it is necessary to compare the curve for the supporting electrolyte with the curve obtained after addition of a surface-active agent or a depolariser. In the potential range in which the substance is adsorbed on the electrode surface, the capacitance of the electrode decreases and, in accordance with Eqn. (3), the quantity dE/dt increases. This means that the $dE/dt = f(E)$ curve in this potential range goes beyond the limits of the supporting-electrolyte curve. In contrast, for processes involving electron transfer, as a result of the consumption of current in the reduction (or oxidation) of the depolariser, the curve at potentials more negative (or more positive) than the potential of the incision will lie inside the contour of the pure supporting electrolyte.

A characteristic feature of the oscillographic dE/dt method is that it permits separate observation of capacitive phenomena and processes involving electron transfer, whereas in the $i-E$ method, for example, the capacitive currents and oxidation or reduction currents are often superimposed on one another.

Although the dE/dt method also makes it possible to study the adsorption of organic substances on an electrode surface, the results obtained by this method are for the most part qualitative. The exact dependence of the differential capacitance on potential, characterising the adsorption of a substance, is determined by the method proposed by Frumkin[32].

To obtain a curve with clearly defined extreme points in the oscillographic dE/dt method (Fig. 1), use is made of a d.c. component superimposed on the a.c. component. The magnitude of this d.c. component is not fixed precisely, but depends on the composition and nature of the supporting electrolyte: it is always smaller with alkaline than with acidic solutions. The current density with which the electrode is polarised is given by the expression

$$i = i_0 \sin \omega t + i_1, \qquad (4)$$

where i_0 is the amplitude of the current density and i_1 the magnitude of the d.c. component (per square centimetre of electrode surface).

If i_1 is large, the electrode, being negatively charged, may acquire a potential equal to that at which the cation of the supporting electrolyte is reduced. In this case the $dE/dt = f(E)$ curve becomes a point. To obtain a curve of regular shape, the following theoretical relationship[30,35] should be satisfied

$$|i_1| < \frac{i_0}{2}\sqrt{\frac{T}{2t}},$$

where t is the drop time of the electrode and T the period of the a.c.

According to theoretical calculations, it is impossible to obtain a $dE/dt = f(E)$ curve of regular shape without superposition of a d.c. component if the current density is less than 0.02 A cm^{-2}. This is not always the case, however. This discrepancy is apparently due to the irreversibility of the electrode processes, *e.g.* by the deactivation of the reduction products of the supporting-electrolyte cation; this is shown to a particularly marked degree in solutions of strong acids. In general, there may be two causes of irreversibility: loss of reduction product of the support cation, or loss of the product of the anodic dissolution of mercury. According to the Nernst equation, in the first case there is a displacement of the electrode potential towards positive values; this displacement may be compensated for by a direct component which charges the electrode to negative potentials. The second factor brings about a displacement of potential in the opposite direction but is less marked than the first. The influence of the d.c. component on the shape of the oscillogram has been examined in more detail by Kalvoda[8] and Micka[30,31].

In oscillographic polarography the current passing through the polarographic cell is several times greater than the current in classical polarography. Thus in order to diminish the potential drop iR in the solution, it is necessary to use concentrated (1 M) supporting electrolytes. In the dE/dt method the potential drop is compensated for by a special assembly[36], which makes it possible to use, for the study of organic compounds, solutions with a high ohmic resistance (0.01 M electrolyte in the presence of an organic solvent).

In addition to the dE/dt method, there are other oscillographic methods, in particular the $i-E$ method. The appearance of the $i = f(E)$ curves depends on the form of the pulse applied to the cell. In the method which has now found widest use in organic oscillography, a triangular voltage pulse is applied to the cell. This method can be used to study both reducing and oxidising processes involving organic substances at an electrode. In the absence of electrochemically active compounds, the $i = f(E)$ curve has the form shown in Fig. 2 and, as in the case of the $dE/dt = f(E)$ curve, consists of two branches. If the solution contains a depolariser, the oscillogram shows peaks at potentials characteristic of the substance.

It has not yet been possible to obtain an analytical equation for the oscillographic $i = f(E)$ curve even for the simplest case, with allowance for only linear diffusion. Ševčik[37] obtained an equation by an approximate method, using the Laplace transformation. Randles[38] obtained a solution by a graphical method. Their solutions differ slightly from one another. Recently, Gokhshtein[39] has derived a general equation for reversible processes with cathodic and anodic polarisation.

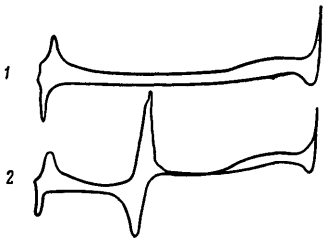


Fig.2. Oscillographic $i = f(E)$ curves for:
1) 0.2 M NaOH solution;
2) 3×10^{-4} M benzil in the same solution.

According to Delahay[6] the magnitude of the current i_p at the potential of the peak is given for reversible processes by the equation

$$i_p = 2.72 \times 10^5 n^{3/2} A D^{1/2} V^{1/2} C, \quad (5)$$

where A is the area of the cathode (in cm^2), D the diffusion coefficient, V the rate of change of potential ($V\ s^{-1}$), C the concentration of depolariser, and n the number of electrons taking part in the electrode reaction.

Unlike the case of the dE/dt method, the direct component of the current in the oscillographic $i-E$ method has a definite value, which influences the form of the resulting $i = f(E)$ curve. The presence in solution of surface-active substances which are adsorbed on the electrode is revealed on the $i = f(E)$ curves in the form of adsorption and desorption peaks, in contrast to the incisions on the $dE/dt = f(E)$ curves. The possibility of studying capacitive effects by the $i-E$ method has been discussed many times[40-42]. This question is discussed in more detail below.

The influence of atmospheric oxygen dissolved in the electrolyte in oscillographic polarography differs from that in ordinary polarography. To obtain the classical polarogram for a solution, preliminary removal of oxygen is necessary, but this is not essential in oscillographic polarography. This is of considerable value in the study of organic substances and reactions taking place at the moment of their dissolution.

III. USE OF OSCILLOGRAPHIC POLAROGRAPHY IN ORGANIC CHEMISTRY

Up to the present, the main attention in oscillographic polarography has been directed to the development of convenient analytical methods for the determination of various substances. It has been found that oscillographic polarography makes possible the quantitative determination of complex organic compounds such as the alkaloids of the tropane group[43-46] (cocaine, atropine, homatropine), the veratrine alkaloids[47], and a number of other alkaloids[48,49] and amino-acids[50] which cannot be determined quantitatively by classical polarography. Recently, however, oscillographic polarography has begun to be used not only for analytical purposes but also for the solution of various theoretical problems in organic chemistry. The number of substances which have been studied by oscillographic polarography is still small, so that systematic presentation of the results according to the classes of organic compound would not reveal clearly the advantage of oscillographic polarography in the study of organic substances. There are three fields in which oscillographic polarography is being used successfully for the study of organic substances — (1) study of the physicochemical properties of compounds, (2) study of the mechanism of electrode processes involving organic substances, and (3) study of chemical reactions and structural problems.

1. Study of Some Physicochemical Properties of Organic Compounds

In the previous Section it was shown that the adsorption of organic substances at an electrode–solution interface is revealed on the oscillographic curves in the form of incisions or peaks. The surface activity of a substance depends on its physicochemical properties, so that oscillographic polarography makes it possible to study certain physicochemical properties of organic compounds. The number of oscillographic studies devoted to this problem, however, is still small.

In the first experiments on oscillographic polarography, Heyrovský and his coworkers[51] found that distinct capacitive effects are given by substances which are sparingly soluble in the supporting electrolyte. Thus, alkaline solutions of pyridine and its homologues form adsorption films on a dropping mercury electrode; no adsorption is observed in the case of solutions in mineral acids. Aliphatic acids, on the other hand, are adsorbed on the electrode surface, giving capacitive effects on the oscillograms for acidic solutions. Their alkaline solutions are oscillographically inactive. Heyrovský and his coworkers found that adsorption films are formed by alcohols, phenyl salicylate, and camphor. Matiaš,[52] in a study of oscillographic $dE/dt = f(E)$ curves, also detected the adsorption of certain aliphatic alcohols and its influence on the reduction of cations. For each homologue studied, Matiaš found the potentials of adsorption and desorption at different concentrations in the solution.

The capacity effects produced by various alcohols on the $i = f(E)$ curves were studied by Loveland and Elving[53,54]. In the case of saturated solutions of pentanols, both branches of the oscillogram showed two peaks corresponding to adsorption and desorption of the alcohol molecules at the electrode surface. For n-hexanol, however, the authors observed three peaks on each branch, and for heptanol and octanol they observed four peaks. The same alcohols in the colloidal state gave two peaks on each branch of the oscillographic $i = f(E)$ curve. After removal of air from the colloidal solution, the oscillograms acquired the form characteristic of saturated solutions of the alcohols. On the basis of their results, Loveland and Elving concluded that mono- and bi-molecular films of the alcohols may be formed at the mercury–solution interface. The bimolecular film is revealed on the oscillogram by four adsorption and desorption peaks. With increase in the number of carbon atoms in the alcohol molecule, this tendency to form a bimolecular adsorbed film increases, and Loveland and Elving suggest that this is related to the solubility and dielectric properties of the alcohols in aqueous medium. The same authors[55], in a study of the adsorption of the eight isomeric pentanols, found that the difference between the potentials of the adsorption and desorption peaks appears to be related to the structure of the hydrocarbon radical of the alcohol molecule: the greater the degree of branching of this radical, the smaller the observed difference in the potential. From this it follows that the surface activity is determined by the chemical structure of the substance.

A detailed study of the adsorption characteristics of various aliphatic alcohols by the oscillographic dE/dt method has been made by Kalvoda [56]. Methanol and ethanol bring about only slight deformation of the curve for 1 M NaOH solution. With increase in the number of carbon atoms in the aliphatic alcohol molecule, however, the depth of the capacitive incisions increases (Fig. 3), and the capacity phenomena are observed at lower alcohol concentrations. The relative adsorbability of the individual alcohols was determined by means of two $dE/dt = f(E)$ curves for solutions with different concentrations of the alcohols being compared, for which the depth of the incisions was the same. The adsorption characteristics of aliphatic alcohols are compared with some of their physicochemical properties in Table 2. Kalvoda found that the slope of the straight line representing the potential of the capactive incision as a function of the logarithm of the concentration is determined by the nature of the alcohol molecule, and decreases with increase in the length of the aliphatic chain (Fig. 4).

It can be seen from Fig. 3 that adsorption may be revealed on the oscillographic $dE/dt = f(E)$ curves either as sharp incisions or as oval depressions on both cathodic and anodic branches of the curves. The shape of these incisions apparently depends on the rate of the adsorption process. In his study of the adsorption of aliphatic alcohols, Kalvoda [56] derived experimentally a simple rule, by means of which it is possible to distinguish a capacitive incision

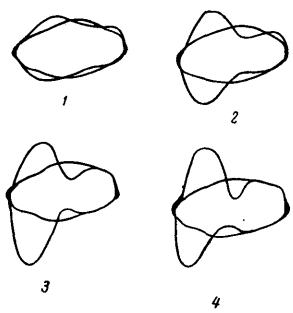


Fig. 3. Curves of $dE/dt = f(E)$ for alcoholic solutions:
1) 20% methanol in 0.8 M NaOH;
2) 20% ethanol in 0.8 M NaOH;
3) 0.5 M propanol in 1 M NaOH;
4) 0.008 M hexanol in 1 M NaOH.
The curves for the supporting electrolytes are given for comparison [56].

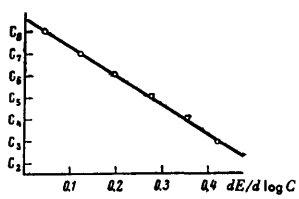


Fig. 4. Dependence of $dE/d \log C$ on the number of carbon atoms in the aliphatic radical of alcohols [56].

TABLE 2.

R	C_2H_5	n-C_3H_7	s-C_4H_9	iso-C_4H_9	n-C_4H_9	n-C_5H_{11}	n-C_6H_{13}	n-C_7H_{15}
Adsorption activity	1/1500	1/75	1/40	1/40	1/30	1/7	1	4
Concentration at which a detectable incision appears, M	1	$1.5 \cdot 10^{-1}$	$4 \cdot 10^{-2}$	$2 \cdot 10^{-2}$	$2 \cdot 10^{-2}$	$5 \cdot 10^{-3}$	$1.5 \cdot 10^{-3}$	$3.5 \cdot 10^{-4}$
Solubility of alcohol, g per 100 g H_2O	∞	∞	12.5	9.5	7.9	2.7	0.52	0.09
Boiling point, °C	78.3	97.2	99.5	108	117	138	155.8	174

from one corresponding to an electrochemical reaction in which electrons take part. With increase in the concentration of the substance studied to 0.01 M or 0.1 M, there will be no sudden break in the $dE/dt = f(E)$ curve at the potential of a capacitive incision. At the same time, the magnitude of the direct component of the current will have no influence on the shape of the incision, since in the case of capacitive processes no current is used up in electrolysis. In the case of incisions produced by electrolytic reduction or oxidation, however, increase in the concentration of the substance to 0.01 M causes a sudden break in the $dE/dt = f(E)$ curve at the potential of the incision, since further charging of the dropping electrode becomes impossible as all the electricity is used up in the electrochemical reaction. Kalvoda found that the depth of the capacitive incisions decreases with increase in the concentration of methanol in the solution. The presence of methanol in the solution has no appreciable influence on the depth of the electrochemical incisions.

Kalvoda [56] also studied the adsorption of a number of aromatic hydrocarbons and indole-3-carboxylic acids on a dropping mercury electrode.

Oscillographic polarography with triangular voltage pulses has been used by Gorokhovskii and coworkers [57,58] to investigate the relationship between the physicochemical properties of developers and stabilisers and their photographic action. They find that the appearance of symmetrical cathodic–anodic reversible peaks on the oscillograms for developers corresponds to high developing power. Addition of substances exhibiting a stabilising action in the photographic process produces little change in the capacity of the electrode.

2. Study of the Mechanism of Electrode Processes Involving Organic Substances

The use of oscillographic polarography to study the course of oxidation and reduction processes involving organic compounds is still in an early stage of development. The chief reason for this state of affairs is the difficulty and sometimes the impossibility of interpreting the oscillographic curves, since much work has been carried out under indefinite conditions in unbuffered solutions, and in most cases no comparison has been made between data obtained by oscillographic and classical methods. Only recently has a knowledge of the way in which the nature of a given electrode reaction is revealed on the oscillographic curves made it possible to apply oscillographic polarography to the study of the mechanism of electrochemical processes.

The shape of the oscillographic curve and the dependence of the position of each point on the curve, particularly of the incision or the peak, on the rate of change of potential

are functions of the type of process studied and its characteristic features. These features are related to the fact that the electrochemical process may depend on the diffusion of substance to the electrode or on a preceding chemical reaction or may be accompanied by adsorption. In turn, the processes accompanied by diffusion may be reversible, quasi-reversible, or irreversible. Having proposed the oscillographic method, Heyrovský [59] used it to study the reversibility of the reduction of a number of substances. The reversibility of an electrode process may be assessed from the relative positions of the incisions or peaks on the cathodic and anodic branches of the oscillogram.

It should be noted that the term "oscillographic reversibility" does not mean "polarographic reversibility". Usually, reversibility characterises the rapidity of a process studied by a definite method. In the case of "polarographic reversibility" the rapidity of a process is defined by the coincidence of the half-wave potentials of reduced and oxidised forms and by the shape of the polarographic wave. In the case of "oscillographic reversibility", however, the cathodic or anodic incisions or peaks should appear at identical potentials, and their shapes and depths should be approximately the same. If the potentials of the incisions or peaks are different or if one is completely absent, the process will be partly or completely irreversible. The basic difference between the concepts of reversibility of the electrode process in oscillography and polarography lies in the time required for reduced and oxidised forms of the substance to reach dynamic equilibrium with the electrode potential. In classical polarography the time required for dynamic equilibrium to be established in the electrode reaction is comparable with the drop time of the dropping mercury electrode ($\sim 2-3$ s). Since in oscillographic polarography the entire potential range over which the electrode is polarised is recorded on the screen in 0.01 s, while the electrode process takes $\sim 100-1000$ μs, in this case reversible processes must reach a state of equilibrium in an interval less than 1000 μs. Frequently a system which is reversible in classical polarography is irreversible in oscillographic polarography. There are also processes, however, which behave reversibly in oscillographic polarography but are irreversible in classical polarography. This anomalous behaviour is apparently due to the presence of consecutive electrochemical reactions. These reactions are unable to take place in the short polarisation times of the oscillographic method, but occur in classical polarographic reduction or oxidation, limiting the rapidity with which equilibrium is established. It may thus be said that the meaning of the concept "reversibility" depends on the method of investigation employed, so that the reversibility of a process can give us only approximate information on the rate at which equilibrium is established in the electrode reaction [60].

The number of known cases in which an electrode process controlled by diffusion is reversible is small (benzoquinone, nitrobenzene, etc.). Ševčik [37] showed mathematically that the potentials of the cathodic and anodic peaks of an oscillographically reversible redox system differ from the half-wave potential of the reversibly reduced or oxidised substance by $1.6RT/nF$ V, *i.e.* by $40/n$ mV. The method of oscillographic polarography with linear change in potential makes it possible to establish the nature of the process from the equation [41]

$$\log i_p = \log k + x \log v,$$

where k is the transfer coefficient, v the rate of change of potential, i_p the height of the peak on the oscillogram, and x the rate coefficient, which represents the dependence of the current at the peak on the rate of change of potential. For nitrobenzene $x = 0.5$. Reversible processes are characterised by a sharply defined peak on the oscillogram, but in the case of an irreversible electrode reaction, the peak is "flattened", and its maximum is less sharp. With irreversible processes, the peak height depends on the square root of the rate of application of the potential, giving a rate coefficient of 0.5. For a quasi-reversible electrode process this relationship is more complex, but under certain conditions, and within certain ranges of rate of change of potential, the rate coefficient is less than 0.5. An example of a quasi-reversible process is the reduction of pyrrole-2-aldehyde in dimethylformamide–water medium, for which Cappellina and Pederzini [61] found two peaks on the $i = f(E)$ curve. The position and the height of these peaks depended on the concentration of dimethylformamide in the solution; in the opinion of the authors, this was due either to differences in the solvation of pyrrole-2-aldehyde in dimethylformamide and in water or to a difference in the roles of the protons taking part in the reduction of the molecule. For both peaks the dependence of $\log i_p$ on $\log v$ was linear, and the rate coefficient varied over the range 0.25–0.44.

If the diffusion of depolariser is restricted by the rate of a chemical reaction preceding the electron-transfer stage, the depolariser being formed as a result of this chemical reaction from substances which are not reduced or are reduced at more negative potentials, the oscillographic $dE/dt = f(E)$ curve is L-shaped and the $i = f(E)$ curve is S-shaped (Fig. 5). The $i = f(E)$ oscillogram has no characteristic peak and resembles rather a classical polarogram (Fig. 5). To obtain a clearly defined incision on the $dE/dt = f(E)$ curve it is necessary to increase the concentration of the compound giving the kinetic incision by a factor of 100 relative to the concentration of substance whose electrode reaction is controlled by diffusion. For kinetic processes the rate coefficient is negligibly small: *i.e.* the peak height is almost independent of the rate of change of electrode potential. The temperature coefficient for a kinetic process is comparatively high. With increase in the frequency of the polarisation, the depth of the kinetic incision on the $dE/dt = f(E)$ curve decreases. A kinetic process can be distinguished from a diffusion-controlled process by the different effects of surface-active substances on the shape of this curve. An example is provided by the

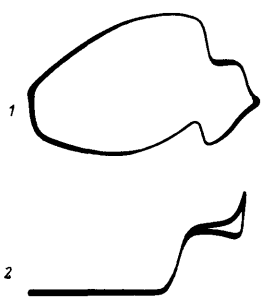


Fig. 5. Oscillograms for a 0.3 M solution of formaldehyde in 1 M NaOH:
1) $dE/dt = f(E)$ curve;
2) $i = f(E)$ curve.

behaviour of neutral solutions of maleic acid in the presence of gelatin. The first incision on the oscillogram corresponds to reduction of the undissociated acid molecule formed as a result of the recombination of an anion with a proton. This kinetic incision disappears after the addition of gelatin. The second incision corresponding to diffusion-controlled reduction of the maleic acid anion, is unaffected by the addition of gelatin[8]. In some cases the presence of surface-active substances (pyridine, alcohols) in solution may lead to retardation of the electrochemical process; this is revealed either by an increase in the difference between the potentials of the cathodic and anodic peaks or incisions (influence on reversibility) or by the splitting of one into several incisions (*e.g.* the influence of pyridine on the reduction of nitrobenzene in alkaline solution[34]). In general, adsorption films may decrease the rates of those electrochemical reactions which involve the transfer of two or more electrons[27].

We have seen above how capacitive effects are revealed on the oscillographic curves and how it is possible to distinguish an adsorption process from a process involving electron transfer. It should be added that a characteristic feature of the adsorption of a depolariser, revealed on the $i = f(E)$ curves, is that the rate coefficient at the peak is always greater than 0.5, but in general is less than 1, and that the peak height varies non-linearly with concentration of surface-active substance. The peak height–concentration curve resembles a Langmuir isotherm. The potential at which the saturation zone is reached, however, increases with rate of application of voltage to the polarographic cell[41].

An example of a catalytic process studied in detail by oscillographic polarography is Brdička's serological reaction[62].

The above characteristic features of electrode processes are used in the interpretation of oscillographic curves on which organic substances can in general give incisions and peaks of all types simultaneously. In oscillographic polarography, however, it is necessary to make allowance for one other important feature which is also the most frequent cause of discrepancy in the results obtained by classical and oscillographic polarography.

In polarography each drop grows at almost constant potential; the maximum change in the electrode potential amounts to ~ 20 mV in the lifetime of one drop. In this case a diffusion layer is formed only by the depolariser and the product of its electrode reaction. On separating from the capillary, the drop carries away the products of the electrode reaction, and the processes taking place on the fresh surface of the next drop are again those which correspond to the electrode potential and which cannot be influenced by the products of the reaction on the preceding drop.

In oscillographic polarography the electrode potential changes over a wide range (usually ~ 2 V) during the lifetime of one drop, and at a polarisation frequency of 50 c/s, for example, this change in electrode potential from 0 to 2 V is repeated 200 times. In the course of this rapid polarisation, the products of an electrode reaction taking place at a definite value of the potential are unable to diffuse into the depth of the solution and remain adjacent to the electrode, where they may either take part in an electrode reaction which takes place at a different potential or be converted chemically to another electrochemically active substance. Thus the oscillograms may show incisions or peaks corresponding to secondary processes involving intermediate compounds formed in the initial electrode reaction at the electrode surface. In classical polarography, the formation and nature of the intermediate compounds are determined from the shape of the waves and from the dependence of the half-wave potential on various factors.

The formation of these intermediate compounds, which are generally referred to as artefacts[63], is characteristic of oscillographic polarography, and in a number of cases has been demonstrated experimentally. The formation of artefacts may take place electrochemically in the course of the electrode reaction on polarisation of the electrode, or as a result of reaction of these intermediate products with one another, *i.e.* by a chemical process. Moreover, the artefacts may be substances produced at the electrode surface as a result of reaction of the intermediate compounds or certain components of the solution with mercury ions formed on positive polarisation of the electrode. These artefacts are reduced, giving corresponding incisions or peaks on the cathodic branches of the oscillographic curves. The polarograms in this case may show anodic waves corresponding to the formation of a compound containing mercury ions. An example is the formation of organomercury compounds with acetylene[64,65] and with certain ketones in alkaline solution[63].

The artefacts may reveal themselves in various ways — by being oxidised, by being reduced, or by being adsorbed on the electrode surface and changing its capacitance. In order to reach unambiguous conclusions in the examination of oscillographic curves, it is necessary to use results obtained by other methods. First of all the results obtained by oscillographic polarography must be compared with those obtained by classical polarography: incisions or peaks on the oscillograms not corresponding to polarographic waves are produced either by adsorption or by artefacts.

If the electrochemical reaction is reversible, the incision or peak of the artefact lies on the opposite branch of the oscillogram at the same potential as the incision or peak of the original depolariser. The oscillogram does not, however, tell us whether the depolariser in solution is in the oxidised form and the artefact on the electrode surface in the reduced form, or *vice versa*; nor does it give the percentages of the depolariser present in the solution in the reduced and oxidised forms. In this case also it is necessary to use data obtained by classical polarography. If two incisions or peaks on an oscillogram lie opposite one another at the same potential on the two branches of the curve, we may again be dealing with two different, independent processes, particularly when the shapes of the incisions or peaks differ.

To identify an intermediate compound taking part in the formation of a redox system, it is possible to use the polarographic method with Kalousek's switch[66-68]. In this method we apply to the dropping mercury electrode a definite auxiliary potential at which the test substance gives the limiting diffusion current, after which the electrode is alternately switched, at a definite frequency, out of this auxiliary circuit and into the polarograph. For example, if the compound is reduced reversibly at a dropping mercury electrode, Kalousek's switch can be used to obtain the anodic wave for the oxidation of the resulting intermediate compound at the same potential. An advantage of this method is that the frequency used in this case is lower than that of the ordinary oscillographic method based on the use of a.c. This simplifies considerably the instrumentation of the method. It has recently been shown[68] that, in work

with this switch, it is necessary to make allowance for the charging currents, which in this case reach higher values than in ordinary polarography, and depend on the auxiliary potential. If the compound being studied is adsorbed on the electrode surface, it is possible, by applying an auxiliary potential at which almost complete desorption of the substance takes place (*e.g.* -2 V), to record its adsorption wave at the potential of its adsorption. The height of this wave will depend both on the auxiliary potential and on the frequency of switching (Fig. 6). This method will probably find further application in the interpretation of oscillograms and the study of the adsorption of organic substances.

To identify the artefacts formed in the course of irreversible electrochemical reactions, it is necessary to follow the influence of the d.c. component on the shape of the oscillographic curve. If by varying the d.c. component we polarise the electrode in such a way that its potential does not reach the value at which the primary electrode reaction takes place, the incision or peak corresponding to the artefact will disappear, since in this case no intermediate product will be formed at the electrode. To investigate the nature of the artefact, it is also necessary to study the influence of the composition of the support and the concentration of the base electrolyte on the shape of the oscillogram. With a change in the support composition, it is possible, by adding a polarographically active electrolyte in excess, to determine the potential range in which formation of the artefact takes place and also to determine which of the support components is involved. For example, carbon disulphide gives incisions on the $dE/dt = f(E)$ curve at positive potentials only when the electrode potential reaches -2 V. When the solution contains an excess of zinc ions (concentration > 0.01 M), the CS_2 incisions disappear, since the electrode potential in this case[8,63] is slightly greater than -1 V, so that reduction of carbon disulphide with the formation of S^{2-} ions, which is responsible for the appearance of incisions at positive potentials, does not take place. Analogous phenomena have also been observed in the case of penicillin[8].

Valuable information on the mechanism of an electrode reaction can be obtained by means of the so-called "first curves".[69,70] These curves indicate whether the artefacts are formed after the first cycle or during repetition of the polarisation cycles. The capacitive incisions are often more clearly defined on the first curves than on the multiwave oscillogram. Kalvoda[56] has observed a similar phenomenon for aliphatic alcohols. If capacitive effects are excluded, the first curves obtained by the oscillographic method with a.c. correspond most closely to the polarographic waves, since artefacts are not revealed on these curves. The concept of "first curves" in this sense naturally relates only to the cathodic branch of the oscillogram.

The use of a jet electrode may be extremely valuable in the study of electrochemical processes involving organic substances. Recently, an electrode of original design has been developed with which the surface area of the jet is independent of the quantity of solution studied[71]. With the rapid renewal of the surface of the jet electrode, products of the electrochemical reaction are unable to concentrate in the layer next to the electrode and interact to form artefacts, so that the oscillographic curves obtained with a jet electrode generally have a simpler shape than the curves obtained for the same solution with a dropping electrode. The jet electrode may reveal only very readily formed artefacts such as organomercury compounds.

In cases in which the products of the electrode reaction may exert a retarding influence on the primary electrochemical process, the incisions corresponding to the primary process are more clearly defined on the curves obtained with a jet electrode than on the curves recorded at a dropping mercury electrode. For example, the incisions corresponding to the reduction of carbon disulphide are hardly detectable on the oscillograms obtained at a dropping electrode. In the case of the jet electrode, these incisions are much more clearly defined, the cathodic incision for the artefact being almost non-existent (Fig. 7).

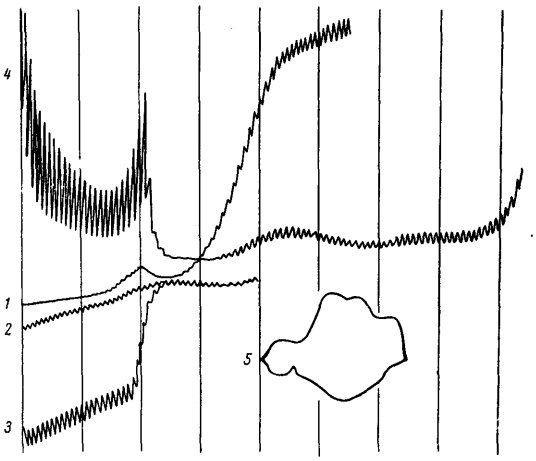


Fig. 6. Curves for a 10^{-4} M solution of tetraphenylethylene glycol in 50% methanol, 0.5 M H_2SO_4; origin of curves 0.0 V; 200 mV along the abscissa; Yanagimoto PA-101 polarograph (1960); sulphate reference electrode:
1) classical polarogram;
2) polarogram recorded by means of a Kalousek switch, auxiliary potential -0.6 V;
3) the same curve for a potential of -1.2 V;
4) a.c. polarogram;
5) oscillographic $dE/dt = f(E)$ curve.

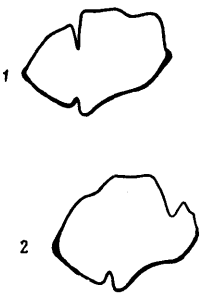


Fig. 7. Oscillographic $dE/dt = f(E)$ curves for a 5×10^{-4} M solution of carbon disulphide in acetate buffer at:
1) dropping mercury electrode;
2) jet electrode[8].

If intermediate compounds are formed in sufficient quantity during the electrode reaction, they can be detected by means of a mercury electrode with a small surface area, such as the hanging drop[23-25], and the curves can be recorded by the usual polarographic method.

A typical example of a reaction involving the formation of various intermediate compounds is the reduction of nitrobenzene[72], whose electrochemical behaviour has been studied by many workers. Nitrobenzene was used in the first oscillopolarographic measurements by Heyrovský[3,5]. From the depth of the cathodic incision on the oscillographic curve for nitrobenzene in alkaline solution it was calculated that its electrolytic reduction is a four-electron process. When a surface-active substance, *e.g.* pyridine, is added to a solution of nitrobenzene, the four-electron incision for nitrobenzene is split into two. Of the resulting cathodic incisions, the first corresponds to a one-electron reduction, and the second to a three-electron process. The sum of the areas of the two incisions is equal to the area of the initial four-electron incision. Thus the four-electron reduction of nitrobenzene in alkaline solution in the presence of a surface-active substance takes place in stages: the molecule first takes up an electron to form a radical-anion

$$\left(C_6H_5\overset{+}{N}\!<\!\begin{matrix}O^-\\O\end{matrix}\right)^-,$$

which is reduced to the hydroxylamine derivative only at more negative potentials. It should be noted that nitromethane under the conditions of oscillographic polarography is reduced according to a four-electron mechanism[5]. The incision for nitrobenzene is much sharper than that for nitromethane, however, and from this it was concluded that the nitromethane molecule adds on four electrons successively, not rapidly and simultaneously as in the case of the nitrobenzene molecule. Kemula and Kublik attempted to follow the formation of artefacts during the reduction of nitrobenzene by using the method of cyclic voltammetry with a hanging mercury drop[24]. This method, as proposed by Kemula and his coworkers and by Vogel[25], is essentially analogous to oscillographic polarography with a low rate of application of potential of symmetrical sawtooth form. It is of interest that Delahay[6] classifies oscillographic polarography in which $i = f(E)$ curves are studied as a method of multiwave voltammetry with continuously changing potential. Thus by means of cyclic voltammetry it is possible to change from classical polarography to oscillographic polarography and conversely; this is of particular importance in the study of the mechanism of electrochemical processes involving organic compounds.

In Kemula and Vogel's method, using a hanging mercury drop as electrode, the products of the primary electrode process and of secondary reactions remain close to the electrode and may be determined. An analogy is also observed in the case of preparative electrolysis at a mercury microelectrode. An advantage of the hanging drop compared with the latter method is that the products of the electrode reaction can be studied directly, in the same solution and at the same electrode.

During polarographic reduction, nitrobenzene is converted into phenylhydroxylamine. During polarisation of the hanging drop in cyclic voltammetry, the nitro-group is likewise reduced to the hydroxyamino-group at the surface of the microelectrode. During the reverse polarisation, the phenylhydroxylamine formed is oxidised on the electrode surface to nitrosobenzene at -0.22 V (relative to the saturated calomel electrode, s.c.e.). In the second cycle, nitrosobenzene is reduced to phenylhydroxylamine. Kemula and Kublik[23] found that the redox potential of the reversible nitrosobenzene–phenylhydroxylamine system is displaced to more negative values with increase in the pH of the solution. In strongly alkaline solutions, nitrosobenzene reacts with phenylhydroxylamine to form azoxybenzene; the peak corresponding to reduction of the nitroso-group disappears, and the peak corresponding to reduction of the nitro-group forms an inflection. In Kemula and Kublik's opinion this inflection is due to the influence of the resulting surface-active substance, azoxybenzene; this was confirmed by analysis of the cyclic-voltammetric curves for a mixture of azoxybenzene and nitrobenzene. In this case a new reversible redox system is produced:

$$C_6H_5NO_2 + e \rightleftarrows (C_6H_5\dot{N}O_2)^-.$$

If during polarisation of the electrode the potential does not reach the value at which reduction of the nitro-group takes place, the nitrobenzene–phenylhydroxylamine system is not formed. Kemula and Kublik also tried to explain the nature of some of the incisions on the $dE/dt = f(E)$ oscillographic polarograms for nitrobenzene solutions. They attributed the decrease in the depth of the incisions corresponding to the nitrobenzene–phenylhydroxylamine system with increase in the direct component of the current to a change in the mechanism of reduction of the nitro-group. If the electrode polarisation reached -2.0 V, the nitrobenzene is reduced to aniline, as a result of which the incision for phenylhydroxylamine and hence nitrobenzene decreases. With increase in the pH of the solution the $dE/dt = f(E)$ curves showed new incisions, whose nature could not be determined.

The oscillogram for an alkaline solution of nitrobenzene is very complex (Fig. 8). Of the six incisions on the curve, only one corresponds to the polarographic wave for nitrobenzene; the other incisions correspond to various intermediate compounds.

Volke[73] made a detailed study of the oscillopolarographic behaviour of nitrobenzene over a wide pH range in order to compare data on the reduction of nitrobenzene with data obtained in an oscillographic study of isomeric nitropyridines[74], which also, like nitrobenzene, gave complex

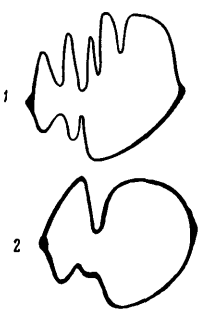


Fig. 8. Curves of $dE/dt = f(E)$ for a 10^{-3} M solution of nitrobenzene in 1 M KOH at:
1) dropping electrode;
2) jet electrode[34].

curves. He showed in the case of nitrobenzene how oscillographic polarography can be used to study the mechanism of an electrochemical reduction and to identify the intermediate products and the sequence of their reactions with one another.

Since the products formed during the electrolytic reduction of nitrobenzene are known, Volke first of all studied the oscillopolarographic behaviour of these compounds and determined the potentials of their incisions. The nitrobenzene–phenylhydroxylamine system was studied. In contrast to the polarographic results, the oscillographic $dE/dt = f(E)$ curve in the potential range where polarographic reduction of phenylhydroxylamine takes place showed no clearly defined incision; the presence of an anodic incision on the curve indicated that the phenylhydroxylamine is oxidised at the dropping mercury electrode. The oscillograms for alkaline solutions of phenylhydroxylamine were complex and very similar to the curves for nitrobenzene under the same conditions (Fig. 8). It was found that the shape of the curves changed with time; the depth of the incision for the nitrobenzene–phenylhydroxylamine redox system changed particularly rapidly in the presence of atmospheric oxygen, and new incisions appeared. In the case of a jet electrode, the curve for phenylhydroxylamine in alkaline solution was again complex, indicating that chemical changes take place in the phenylhydroxylamine solution. Volke also found that at pH < 2 the azobenzene–hydrazobenzene redox system is reversible; this was confirmed by polarography with a Kalousek switch. Azoxybenzene shows irreversible behaviour during electrolytic reduction; the number of incisions on the oscillogram depends on the concentration of depolariser. On the basis of a study of the first curves for azoxybenzene, Volke concluded that, as in classical polarography, azoxybenzene was first reduced with the attachment of four electrons, and four protons to form hydrazobenzene, which gave capacitive effects on the curves. During the reverse polarisation in the first cycle, hydrazobenzene was oxidised, with the participation of two electrons, to azobenzene, which in the second and subsequent cycles was reduced to hydrazobenzene and gave a corresponding incision.

$$C_6H_5-\underset{\underset{O}{\downarrow}}{N}=N-C_6H_5+4e+4H^+ \longrightarrow C_6H_5-NH-NH-C_6H_5+H_2O,$$

$$C_6H_5-NH-NH-C_6H_5 \longrightarrow C_6H_5-N=N-C_6H_5+2e+2H^+,$$

$$C_6H_5-N=N-C_6H_5+2e+2H^+ \longrightarrow C_6H_5-NH-NH-C_6H_5.$$

Detailed study of the oscillopolarographic behaviour of these redox systems enabled Volke to explain the complex curves for nitrobenzene. According to the polarographic data, the electrochemical reduction of nitrobenzene in acidic and neutral solutions takes place in an essentially simple fashion and is represented by the following scheme:

$$C_6H_5NO_2+4e+4H^+ \longrightarrow C_6H_5-NHOH+H_2O,$$

$$C_6H_5NHOH \rightleftarrows C_6H_5NO+2e+2H^+.$$

This is confirmed by data on the effect on the depth of the incisions of adding the corresponding intermediate compounds, by the first curves, by the influence of the d.c. component on the shape of the oscillogram, and by the curves obtained with a jet electrode.

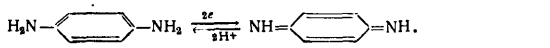
With increase in the pH of the solution there is an increase in the rate of the reaction between phenylhydroxylamine and the nitrosobenzene which is formed as an artefact at the electrode surface, with the production of azoxybenzene:

$$C_6H_5NHOH+C_6H_5NO \longrightarrow C_6H_5-\underset{\underset{O}{\downarrow}}{N}=N-C_6H_5+H_2O.$$

Thus identification of the incisions on the curves for nitrobenzene enabled Volke to explain its electrochemical behaviour. Like Kemula and Kublik[23], Volke found that azoxybenzene influenced the reduction of nitrobenzene and assumed that the latter forms the polarographically active $C_6H_5\dot{N}O_2^-$ radical in the presence of azoxybenzene.

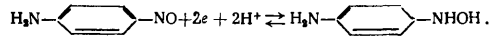
Our study[75] of the oscillopolarographic behaviour of the semicarbazones and thiosemicarbazones of isomeric nitrobenzaldehydes has shown the marked similarity between the behaviour of the nitro-group in these compounds and in nitropyridines and nitrobenzene[73,74]. The nitro-group in these semicarbazones and thiosemicarbazones is apparently reduced by a mechanism similar to that for nitrobenzene.

By means of cyclic voltammetry with a hanging mercury drop, Kemula and Kublik[24] detected the formation of a number of intermediate products in the reduction of *p*-nitroaniline in 0.1 M potassium hydroxide solution. In the first drop-polarisation cycle, *p*-nitroaniline is reduced to *p*-phenylenediamine, which is then oxidised on the electrode surface to *p*-benzoquinonediimine and gives the corresponding oxidation peak at the end of the cycle. Reduction of the diimine takes place in the second cycle, this redox system being reversible.

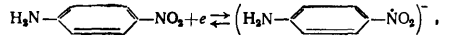


These conclusions were confirmed in a study, under the same conditions, of *p*-phenylenediamine, whose oscillograms showed peaks identical to the positive peaks for *p*-nitroaniline on the cyclic-voltammetric curves. Later, Olson *et al.*[76] obtained similar results using a graphite paste electrode instead of a hanging mercury drop.

Of the five incisions on the $dE/dt = f(E)$ curve for *p*-nitroaniline, only three correspond to the three peaks on the cyclic-voltammetric curve for this substance. Kemula and Kublik[24] suggested that the additional pair of incisions on the oscillogram belong to a new redox system formed under the conditions of oscillographic polarography:



Addition of camphor, which brings about splitting of the wave for *p*-nitroaniline in alkaline medium, leads to the appearance of a second peak on Kemula's cyclic curve, apparently owing to the formation of a reversible redox system at -0.8 V (s.c.e.)



similar to the system produced in the case of unsubstituted nitrobenzene under the same conditions.

In the cases examined, the artefacts formed under oscillographic conditions took part in various reactions involving electron transfer and thus revealed themselves on the oscillograms. The substances and artefacts studied may, however, give various capacitive effects on the oscillographic curves, being adsorbed on the electrode surface.

In the study of these capacitive phenomena, a marked analogy may be observed between the oscillographic curves for the substances studied and their a.c. polarograms, or as they are still called, tensametric curves. This method of polarography with a.c. was first proposed by Frumkin[77] and used to study adsorption phenomena at a dropping mercury electrode. The method consists in measurement of an alternating current which passes through the cell and depends on the electrode potential, the latter being altered in the usual polarographic manner.

The a.c. polarogram resembles a differential polarogram, but whereas on the latter a maximum corresponds to a definite electrode reaction involving reduction of a component of the solution being studied, the position of a maximum on the a.c. polarogram is determined not only by this reaction but also by capacitive phenomena at the electrode surface–solution interface. If no reduction process takes place at the electrode, a so-called tensametric curve is obtained, analogous to a capacitance–potential curve[78]. Recently, a.c. polarography has been widely used, chiefly in organic polarography. The general principles of this method have been described in a number of papers[6,78,79]. The a.c. polarogram often corresponds more or less exactly to the oscillographic curve, and hence makes it possible to interpret the latter. Curves obtained by different methods for phenyl trityl ketone (Fig. 6) show that this compound is first adsorbed on the surface of the dropping electrode, after which the adsorbed form is reduced, and the product is desorbed from the electrode surface.

The intermediate compounds formed during the rapid and repeated polarisation of the electrode complicate interpretation of the oscillograms; the use of a jet electrode instead of a dropping electrode in oscillographic polarography has therefore been recently recommended. However, the possibility of recording oxidation and reduction reactions in rapid succession and of identifying the resulting intermediate compounds means that in the near future oscillographic polarography with a dropping electrode will become an effective method of studying the mechanism of electrochemical processes involving organic substances. In this connection oscillographic polarography may be of considerable assistance in the industrial electrolytic synthesis of organic compounds. One example is of interest. It has previously been pointed out[80,81] that the electrochemical reduction of acetone, ethyl methyl ketone, phenylacetone, acetophenone, cyclopentanone, cyclohexanone, and benzaldehyde at a mercury cathode is accompanied by formation of the corresponding organomercury compounds. These compounds were isolated from solution when reduction was complete.

In a review of work on the oscillographic polarography of ketones, Kalvoda[82] drew attention to the anodic incisions at positive potentials on the oscillographic $dE/dt = f(E)$ curves for a number of carbonyl compounds, particularly acetone and cyclohexanone. These incisions are observed only with acidic solutions of ketones; they become smaller with increase in the pH of the solution, and are almost non-existent at pH ~ 3.0. The anodic incisions for ketones appear only when the negative potential of the electrode exceeds -1.3 V, *i.e.* when hydrogen is liberated. Thus the curve, for a sulphuric-acid solution of acetone, recorded with a hanging drop and reverse polarisation of the electrode from -0.3 V, contains no peaks. When a potential of -1.5 V is applied to the electrode for 20–25 s, however, the same curve shows a deep peak corresponding to oxidation of the resulting product at a potential of about 0 V. With decrease in the d.c. component, the anodic incisions for the ketones disappear. Hence it is concluded that the anodic incisions for acetone correspond to artefacts formed at negative potentials. Known products of the reduction of acetone, such as pinacol, isopropanol, and propene, do not give anodic incisions on the corresponding oscillograms; but the product which is isolated during the preparative electrolysis of acetone at a mercury cathode and which contains an organomercury compound, probably diisopropylmercury, gives analogous anodic incisions. In the preparative reduction of cyclohexanone at a mercury cathode, Kalvoda isolated dicyclohexylmercury, which also gave anodic incisions analogous to those on the curve for a sulphuric acid solution of cyclohexanone. It has thus been shown that the reduction of certain carbonyl compounds at a mercury electrode involves the formation of an artefact in which the surface of the electrode itself participates. The mechanism of this process is not yet clear.

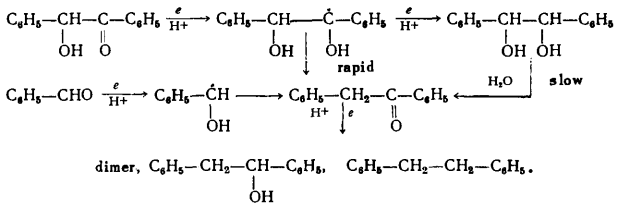
In a study of benzaldehyde in buffer solutions by the oscillographic $i-E$ method, Valenta[83] also detected anodic peaks at positive potentials on the oscillograms. In this case also the anodic peak is apparently due to oxidation of an organomercury compound formed at negative potentials.

The following analogy can be drawn between oscillographic polarography with a.c. and macroelectrolysis used for preparative purposes. In the preparative electrolysis of organic compounds on the industrial scale, electrolytic reduction with controlled current is most frequently used. Electrolysis in this case takes place either at the reduction potential of the substance or at the deposition potential of the cation of the supporting electrolyte. The yield of product, however, depends on a number of factors (electrode material, current density, temperature, composition of solution, etc.). In general, electrolysis in this case gives several substances, some of which are side-products. A somewhat analogous phenomenon is observed during the reduction of a substance under conditions of oscillographic polarography, since the product formed at one potential may react further at the electrode at a different potential. Under the conditions of electrolysis with controlled potential (analogous to classical polarography) it is sometimes possible to obtain a product of maximum purity, but from the economic viewpoint this type of synthesis is not suitable for industrial use. Moreover, the range of substances which may be reduced at controlled potential is much smaller than the range of compounds which react at controlled current. Oscillographic polarography with a.c. can be used to study phenomena occurring under conditions of preparative electrolytic synthesis in order to select the optimum conditions for this process. Thus Kalvoda[82] used oscillographic polarography to find the conditions under which the formation of organomercury compounds by the reduction of ketones at a mercury cathode takes place in highest yield.

One group of substances for which it has been possible, by means of oscillographic polarography, to follow electrochemical reactions and to compare these with the results of electrolysis at controlled current, consists of the aromatic carbonyl compounds[84,85]. It is found that under conditions of oscillographic polarography the reduc-

tion product of acetophenone, the pinacol, undergoes rearrangement in acidic solutions with the formation of the pinacone. This pinacone rearrangement can be readily followed oscillographically from the appearance of a new incision on the $dE/dt = f(E)$ curve during conversion of the pinacol, if 8 M sulphuric acid is used as support.

Study of the benzil–benzoin–hydrobenzoin–deoxybenzoin system shows that under conditions of oscillographic polarography the following series of reactions can occur:



Benzil on reduction gives an enediol, which is apparently oxidised, being revealed on the oscillogram by a corresponding anodic incision. No appreciable rearrangement of this enediol to benzoin is observed under the conditions studied. The product of the reduction of benzoin is slowly converted as a result of dehydration into deoxybenzoin in acid solutions. Under conditions of oscillographic polarography, however, the formation of deoxybenzoin during the reduction of benzoin may also take place *via* an intermediate radical as shown in the scheme. A characteristic feature of the reduction of benzaldehyde in 1 M H_2SO_4 is the formation of hydrobenzoin; in 8 M H_2SO_4, moreover, dibenzylmercury is formed during its reduction. The above scheme of reactions has been confirmed by an oscillographic study of various synthesised intermediate reduction products and comparison of all the data obtained by the different methods used in the interpretation of the oscillographic polarograms.

It may therefore be concluded that oscillographic polarography with a.c. can be used for the extremely detailed study of electrochemical processes in which organic substances take part. To obtain successful and convincing results, however, certain rules and working conditions must be observed. In the first place, it is necessary to use buffer solutions with different pH values as in ordinary polarography. It is also important to study the influence of the concentration of substance on the oscillopolarographic characteristics. Sometimes the nature of an incision can be determined from its shape, which changes during growth of the drop; in some cases the appearance or disappearance of new peaks or incisions is observed during growth of the drop. These phenomena may be due to the fact that during the increase in the drop surface, the current density at the surface changes. It is thus also necessary to study the influence of current density on the shape of the oscillographic curve.

3. Study of the Structure of Organic Compounds and Their Chemical Reactions

It was pointed out above that the adsorption of organic substances, particularly alcohols, is related to their molecular structure[54-56], so that the latter can be studied by oscillographic polarography.

The ease with which a depolariser accepts or donates electrons during an electrode reaction, and also the tendency for various artefacts to be formed, depend on the chemical structure of the polarographically active compound. Thus by using oscillographic polarography to study the mechanism of an electrode process in which an organic substance takes part, it is possible to reach certain conclusions regarding the reactivity of the compound.

In most cases, compounds which are related structurally are reduced polarographically at similar potentials, so that the compounds cannot be distinguished. Sometimes it is possible to distinguish isomers by classical polarography by making use either of the difference in the influence of substituents or of the difference in the influence of pH on the half-wave potentials of the isomers. In the latter case it is usual to find the pH range in which the difference in the half-wave potentials of the two isomers is a maximum. Since oscillographic polarography has a much higher resolving power than ordinary polarography, the former can be used in a number of cases to distinguish isomers with similar structures. Thus the oscillographic study of a mixture of isomeric nitrophenols was for a long time quoted as an example of the use of oscillography for this purpose[86].

In the study of the oscillopolarographic behaviour of any substance, it is important not only to obtain the oscillographic characteristics of this substance (the number of peaks or incisions on the curve, their potentials, etc.) but also to reach definite conclusions regarding the mechanism of the electrochemical process, which can be studied by the methods examined in the previous Section, and hence conclusions regarding the chemical structure of the compound.

Most papers on the oscillographic polarography of organic compounds published up to 1960 are purely descriptive. They generally give the oscillographic curves for the substances studied in solutions at different pH values and describe the incisions or peaks on the curves; the potentials of these peaks or incisions were not always measured. Although in these papers the polarographic results are often compared with the oscillographic data, the authors seldom reach conclusions regarding the mechanism of the electrode processes and the structure of the organic compounds.

Thus studies have been made of the polarographic and oscillographic behaviour of a number of 1-nitroalkanes[87] at different pH values, various esters of phthalic acid[88], and also tropone and tropolone[89].

The presence of two similar incisions on the cathodic and anodic branches of the $dE/dt = f(E)$ curve for an alkaline solution of benzaldehyde at similar potentials was taken as proof of the reversible reduction of this aldehyde at a dropping mercury electrode[90].

Pleticha[91] made a detailed study of the oscillopolarographic behaviour of butane-2,3-dione over a wide pH range and found that the depth of the corresponding cathodic incision on the $dE/dt = f(E)$ curve decreased in the same way as the height of the polarographic wave for biacetyl at a pH > 7.0. At pH ~ 9.0, biacetyl was detected oscillographically only at a concentration of 0.23 M. The depth of the cathodic incision for biacetyl increases with rise in temperature; this agrees with polarographic data, from which it was concluded that biacetyl molecules are hydrated in aqueous solution. The oscillograms for biacetyl show an anodic incision in addition to the cathodic incision. Since the assumed products of the polarographic reduction of biacetyl, *i.e.* acetoin and the pinacol of biacetyl, are,

according to the author's data, oscillographically inactive, the formation of these reduction products under oscillographic conditions cannot be responsible for the appearance of the anodic incision. Pleticha suggested that the anodic activity of biacetyl may be due to the formation of an unstable diol on reduction:

$$CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-CH_3 + 2e + 2H^+ \longrightarrow CH_3-\underset{\underset{OH}{|}}{C}=\underset{\underset{OH}{|}}{C}-CH_3 .$$

In Pleticha's opinion, this but-2-ene-2,3-diol is revealed anodically before it can be converted into acetone.

Aliphatic ketones containing a carbon–hydrogen bond next to the carbonyl group give only capacitive incisions on the $dE/dt = f(E)$ curves in alkaline solutions, but aromatic carbonyl compounds, in addition, show incisions due to electrolytic reduction[92] so long as the concentration of these substances does not exceed 10^{-4} M. With increase in their concentration in alkaline solution to 0.1 M, however, the oscillographic polarograms show additional cathodic incisions at a potential of about 0 V. These incisions are found on the oscillographic polarograms when the dropping mercury cathode, during charging, acquires the potential of the anodic dissolution of mercury. Incisions at about 0 V are not observed when a platinum cathode is used instead of mercury. Heyrovský[92] has recently shown that these incisions correspond to the formation of organomercury compounds by reaction of the enolic forms of the ketones in alkaline solution with bivalent mercury ions at a potential close to the extreme left-hand point on the $dE/dt = f(E)$ curve.

This reaction is not a sensitive test, since the concentration of enol in alkaline solutions is low; its detection by oscillographic polarography can be used successfully, however, to prove the presence of the $O=\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-H$ group in a molecule.

Urea, urethane, and certain other related compounds give analogous incisions on the $dE/dt = f(E)$ curves at a potential of about 0 V.[92] Dušinsky[93], however, considers that these are capacitive incisions.

The higher aliphatic acids and their esters are polarographically inactive. The oscillographic $dE/dt = f(E)$ curves for these compounds, however, give characteristic incisions[8,34]. The shape of the incisions for alkaline solutions of aliphatic acids is independent of the structure of the acid molecule. Their depth at a given molar concentration of acid, however, depends on the structure, and decreases, for example, with increase in chain length in the sequence $C_{13}H_{27}COOH$ (myristic acid), $C_{15}H_{31}COOH$ (palmitic acid), and $C_{17}H_{35}COOH$ (stearic acid).

It is found that, with aliphatic acids whose molecules contain the same number of carbon atoms, the depth of the oscillographic capacitive incision increases with increase in the number of double bonds in the acid molecule.

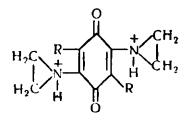
Oscillographic polarography with a.c. has been used by Nygard[94] to study the reversibility of the electrolytic reduction of selenocystine, selenocysteine, and various selenium-containing acids of the type $HOOC(CH_2)_nSeSe(CH_2)_nCOOH$, where n varies from 1 to 4. By comparing their oscillopolarographic behaviour in the pH range 1–12 with that of the corresponding sulphur analogues, he found that rupture of the Se–Se bond takes place more readily than rupture of the disulphide bond during reduction at a dropping mercury electrode. In cyclic disulphides, however, such as 1,2-dithiolancarboxylic acids, in which the five-membered ring is in a state of strain, rupture of the disulphide group takes place about as readily as in the case of aliphatic diselenidodicarboxylic acids.

Unlike trialkyl phosphates whose solutions give only distinct capacitive incisions on the $dE/dt = f(E)$ curves, trialkyl phosphites, at positive potentials on the electrode surface, apparently produce an artefact which forms an intermediate compound with mercury and undergoes the Arbuzov rearrangement[95].

Recently, Damokos[96] made an oscillopolarographic study of alkoxysilanes of the type $Si(OR)_4$ and $SiR'_n(OR)_{4-n}$, where $R = C_2H_5$, C_3H_7, and C_4H_9, and $R' = C_6H_5$ and CH_3. It was found that the oscillopolarographic activity of ethoxysilanes is greater than that of propoxy- and butoxy-silanes, and is proportional to the number of ethoxy-groups in the molecule of the orthosilicic acid derivative. Damokos also compared the adsorption activity of alkoxysilanes with structural factors such as the dipole moment of the molecule (see Table 3).

By using oscillographic polarography with a.c. the Vogel–Kemula hanging mercury drop method, a.c. polarography, and the oscillographic $i-E$ method to study the reversibility of the reduction of certain azo dyes, Horn[97] found that aminoazo-compounds, for which a quinoid structure is possible, are reduced reversibly from alkaline solutions, whereas hydroxyazo-compounds, which cannot form a quinoid structure in alkalis, are reduced irreversibly.

Benzoquinones containing two ethyleneimine rings, of the type



are also reduced reversibly[98]. Using a jet electrode and a special method for the rapid recording of oscillopolarograms, Berg[98] followed the mechanism of the successive splitting of the ethyleneimine rings during their reduction and acid hydrolysis initiated by ultraviolet irradiation.

Of the various heterocyclic compounds, the derivatives of pyridine have been studied in most detail. Volke's work showed that pyridinecarboxylic acids[99] and some of their derivatives[100] exhibiting similar polarographic behaviour are readily distinguished by oscillographic methods.

TABLE 3.

Compound	Depth of incision at 0.006 M, relative units	Dipole moment μ
Ethoxytrimethylsilane	16.5	1.146
Diethoxydimethylsilane	32.0	1.358
Triethoxymethylsilane	48.0	1.678
Ethoxytriphenylsilane	15.5	1.250
Diethoxydiphenylsilane	28.0	—
Triethoxyphenylsilane	43.0	1.538

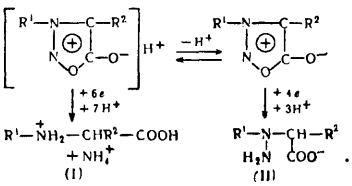
Nicotinamide and the hydrazide of isonicotinic acid are probably reduced by the same mechanism, which differs from that of the reduction of the acids themselves. The anodic incision on the oscillogram for an alkaline solution of the hydrazide of isonicotinic acid is apparently due to reaction between the hydrazino-group of the hydrazide and mercury ions at the dropping mercury electrode, analogous to the reaction of free hydrazine, with formation of a sparingly soluble substance.

The nitriles of all three isomeric pyridinecarboxylic acids are reduced comparatively readily at a dropping mercury electrode [101]. Volke [102] found that with most pyridine derivatives there is a difference in the course of the reduction between the 2- and 4-isomers on the one hand and the 3-isomers on the other. In the case of the cyanopyridines [101], however, there is a considerable difference between the polarographic and oscillographic behaviour of 2-cyanopyridine and that of 4-cyanopyridine. Study of the oscillopolarographic behaviour of the three isomeric pyridinealdehyde oximes [103] showed that the primary electrochemical process is reduction of the azomethine group with formation of the corresponding amine. In weakly acidic acetate solutions under oscillographic conditions, the amines formed may undergo electrochemical deamination at the electrode surface, revealed by an additional cathodic incision on the $dE/dt = f(E)$ curves for the oximes. The aminomethyl group probably reacts at the electrode in the protonated form. Volke confirmed the results of the oscillographic study of the pyridinealdehyde oximes by preparative electrolysis at constant potential.

In a study of the "2,2'-pyridoin–2,2'-pyridil" redox system, Holubek and Volke found that the former compound may not only undergo polarographic reduction but also polarographic oxidation to the di-2-pyridyl diketone. Reduction of the latter, however, yields 2,2'-pyridoin; this was followed oscillopolarographically [104].

Other heterocyclic derivatives of pharmacological importance which have been studied by the oscillographic method include acridines [105], phthalazines, and some pyrimidines [106].

In a study of the course of the polarographic reduction of sydnones in the pH range 0–12, Zuman [107,108] used oscillographic polarography to confirm certain stages in the electrochemical process. Sydnones in acidic solutions are reduced in the protonated form, whereas the non-protonated form is reduced at higher pH values; the half-wave potential of sydnones in weakly alkaline solutions is independent of pH.



The presence of ammonium ions in the reaction mixture after the reduction of sydnones in acidic solutions proves that process (I) occurs. Scheme (II) is confirmed by data obtained in the oscillographic study of sydnones in weakly alkaline solutions. The presence of positive incisions and peaks on the anodic branches of the $dE/dt = f(E)$ and $i = f(E)$ curves in the potential range in which the hydrazino-group reacts at a dropping mercury electrode indicates that the products of the reduction of sydnones at pH > 8 contain a hydrazino-group in the molecule. The fact that the half-wave potential of the sydnones is independent of pH in alkaline solutions enabled Zuman to assume that the potential-determining stage in the reduction of sydnones involves the addition of one electron to the sydnone molecule, and that the attachment of subsequent electrons and protons has no influence on the initial electrochemical act. This hypothesis agrees with the shape of the $dE/dt = f(E)$ curves for the sydnones in weakly alkaline solutions; these curves show several incisions. The formation of a hydrazine derivative according to scheme (II) was established by Zuman by means of polarography with a Kalousek switch and by electrolysis at a controlled potential.

The thiazoles are another group of heterocyclic compounds which have been studied by the oscillographic $i-E$ method [109].

The use of oscillographic polarography to study the chemical properties and reactions of physiologically active compounds and natural products with complex structures is extremely attractive and promising. The analytical oscillographic determination of alkaloids and amino-acids which are polarographically inactive has been mentioned above.

The oscillograms for most alkaloids show characteristic capacitive incisions or peaks, which are most clearly developed in alkaline solutions. In a number of papers on the oscillographic polarography of alkaloids, it has been pointed out that the storage of alkaloid solutions is accompanied by changes which can be followed oscillographically from the decrease in the depth of the incision [8] until, in some cases, the latter disappears completely. This behaviour is shown, for example, by ester alkaloids of the tropane group (Fig. 9).

Dušinsky [110] found that the decrease in the depth of the capacitive incisions for alkaloids during storage of their alkaline solutions is due to hydrolysis, and he used oscillographic polarography to study the kinetics of hydrolysis; it was found that oscillography was in this case superior to all other methods previously used for these purposes.

Dušinsky studied the hydrolysis of atropine (the tropine ester of tropic acid), homatropine (the synthetic tropine ester of mandelic acid), scopolamine (the scopine ester of tropic acid), and cocaine (the methylecgonine ester of benzoic acid) over the concentration range in which the depth of the incisions for the alkaloids varies linearly with concentration. It was found that the hydrolysis products of the alkaloids in this concentration range were oscillographically inactive and did not interfere with study of the hydrolysis. Dušinsky determined the constants and activation energies (Table 4) for the alkaline hydrolysis reactions, using the usual methods of calculation.

Fig. 9. Oscillographic $dE/dt = f(E)$ curves [43] for 6.8×10^{-4} M atropine in 5.5 M NaOH at different lengths of time from addition of the atropine to the solution (s):
1) 50; 2) 75; 3) 130.

TABLE 4.

Alkaloid	$k_{OH^-}(20°)$ litre mole^{-1} s^{-1}	Activation energy, kcal mole^{-1}
Atropine	$5.1 \cdot 10^{-3}$	13.4
Homatropine	$2.7 \cdot 10^{-2}$	12.1
Scopolamine	$1.7 \cdot 10^{-2}$	11.5
Cocaine	$3.7 \cdot 10^{-3}$	11.6

The results obtained by Dušinsky agree with published data on the hydrolysis of these compounds. For example, the fact that the rate of alkaline hydrolysis of homatropine is six times that for atropine is attributed to the inductive effect of the electronegative hydroxy-group of mandelic acid [111].

In lithium hydroxide solution the polarographically inactive narcotine gives a cathodic incision on the oscillographic $dE/dt = f(E)$ curve. The depth of this incision gradually decreases, and a new cathodic incision appears at more positive potentials [112]. This change on the oscillogram for narcotine is due to cleavage of its lactone ring in alkaline solution with formation of a salt of narcotinic acid. Synthesised narcotinic acid in alkaline solutions gives oscillograms with the same incisions as those given by narcotine after cleavage. Similar phenomena were also observed with hydrastine. Changes in the shape of the oscillographic curve with time were established for physostigmine [105], apomorphine [113], and the veratrine alkaloids [47].

Molnar and Molnarova [48] made a detailed study of alkaloids of the quinine group — quinine, quinidine, cinchonine, cinchonidine, euquinine, aristoquinine, hydroquinine, optochine, eucupine, vusine, quinotoxine, and cinchotoxine — in various electrolytes. They found that the vinyl side-group of the quinuclidine ring has no influence on the oscillographic activity and behaviour of the alkaloids studied. The potential of the depolarisation incision of the alkaloid is influenced, however, by the nature of the substituent on the sixth carbon atom of the quinoline nucleus, and this is most marked in alkaline solutions.

The oscillopolarographic behaviour of the alkaloids emetine, *O*-methylpsychotrine, and emetamine, which are derivatives of isoquinoline, has been studied [114]. The oscillopolarographic properties of these alkaloids resemble those of 1,2,3,4-tetrahydropapaverine, 3,4-dihydropapaverine, and papaverine respectively.

Oscillographic polarography has been used to study another group of physiologically active compounds, related to the steroids and hormones. Thus Molnar [115] studied the oscillopolarographic behaviour of some 3- and 17-ketosteroids and their betainylhydrazones. The shape of the oscillographic curve for steroids in acidic aqueous–alcoholic solutions depended on the substituents attached to the steroid framework [116,117].

Of the vitamins, those of the B group have been studied in most detail by oscillographic polarography [118,119]. Pleticha [118] found that in alkaline solutions thiamine shows polarographic and oscillographic behaviour characteristic of compounds containing –S–, –SH, and –S–S– groups in the molecules. By comparing the behaviour of thiamine and cysteine, Pleticha explained the nature of the incisions on the oscillograms for thiamine.

Recently, oscillographic polarography has been used successfully to study the structure of nucleic acids. Paleček [120] found for the first time that nucleotides, nucleosides, and nucleic acid bases are oscillopolarographically active substances, and he used oscillography to study deoxyribonucleic acid (DNA) [121]. In ammonium formate solutions, DNA gives anodic incisions on the $dE/dt = f(E)$ curves at the same potential as deoxyguanylic acid. On this basis, Paleček suggested that the DNA molecule contains deoxyguanylic acid. To prove this he removed adenine and guanine from the DNA molecule by boiling in dilute hydrochloric acid, and studied the resulting apurinic acid by oscillographic polarography in the same ammonium formate solution. He found the apurinic acid to be oscillopolarographically inactive. Paleček also showed that the non-denatured DNA molecule contains deoxycytidylic acid, which, however, is revealed oscillographically only after denaturation of the DNA by boiling in dilute hydrochloric acid. Data obtained in the oscillographic study of deoxyribonucleic acid enabled Paleček to reach conclusions regarding the arrangement of the purine rings of guanine and the pyrimidine rings of cytosine in the DNA molecule.

Paleček's papers [120–124] describe in detail the results of the oscillographic study of nucleic acids and their bases.

The proteins haemoglobin, albumin [125,126], γ-globulin, and fibrinogen [126] have been studied by oscillographic polarography. Mach [126] studied the influence of thermal denaturation of the protein on the position of the incisions on the $dE/at = f(E)$ curves, and also examined the denaturing action of formaldehyde and hydrogen peroxide.

The capacitive effects produced on the $dE/dt = f(E)$ curves by amino-acids and certain peptides, and also the presence of various oscillopolarographically active groups in their molecules, made it possible to study the relationship between the structure and physicohemical properties of these substances and their oscillopolarographic characteristics [127].

Oscillographic polarography can be used to study the kinetics of reactions such as acid and alkaline hydrolysis, whose rates are comparatively low. It has been found possible to use the oscillographic $i-E$ method to characterise qualitatively the slow changes taking place in solutions of developers left to stand in air, to select the optimum conditions for development [128], and also to establish which of the developer oxidation products reacts with the colour components to form dyes under the conditions of colour development [129].

Oscillographic polarography also makes it possible to follow very rapid reactions, whose time of half-reaction may vary from 3 s to 0.01 s. Examples include the coupling of diazotised sulphanilic acid with sulphonated pyrazolone [130] and also the reaction of pyruvic acid with ammonia and the hydrolysis of coumarin [131].

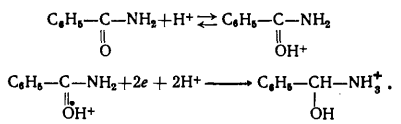
Oscillographic polarography makes it possible to calculate the kinetic rate constants for cases where the depolariser is formed as a result of a chemical reaction preceding the electron transfer stage. Thus Valenta [132] used oscillographic polarography with sawtooth voltage pulses to study the behaviour of formaldehyde in buffer solutions. He found that, at low rates of change of potential, the current is controlled by the rate of dehydration of formaldehyde. With increase in the rate of polarisation of the electrode, the influence of the kinetics of the hydration of formaldehyde diminishes, so that for the central pH range the current is determined by the concentration of free aldehyde present in equilibrium with the hydrated form. The equilibrium concentration of the non-hydrated form

and the dehydration constant of formaldehyde were calculated by comparing the height of the cathodic peak for formaldehyde with the height of the peak for the thallium ion under the same conditions. Volke and Valenta [133] made a similar study of the behaviour of the isomeric formylpyridines and determined their hydration constants from the oscillographic $i = f(E)$ curves.

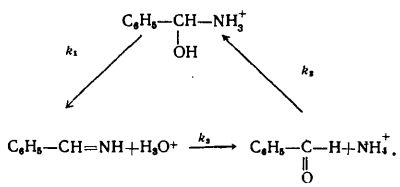
The application of oscillographic polarography to the study of such rapid reactions as the protonation of organic compounds would be extremely interesting, but no work has been carried out on these lines. Recently it has been shown that the "first" oscillopolarographic curves [134], and also, apparently, the hanging mercury drop method, can be used to study "surface" kinetic currents.

In the polarographic study of semicarbazones and thiosemicarbazones it was shown that, on passing from acid solutions to solutions of higher pH, there is an intensification of the kinetic restrictions associated with preliminary protonation of the molecules of the carbonyl derivatives [134]. These correlations, obtained from the results of a study of the semicarbazones and thiosemicarbazones based on current–time curves at the potential of the limiting current, were confirmed qualitatively by oscillographic polarography. The $dE/dt = f(E)$ curves for acidic solutions of these substances show sharp incisions whose shape corresponds to the diffusion character of their reduction. With increase in the pH of the solution, the depth of these incisions decreases, and they gradually approach the L-shaped form typical of a kinetic process. When 0.05% of gelatin is added to the solution, the incisions on the $dE/dt = f(E)$ curves for the semicarbazones and thiosemicarbazones almost disappear, again confirming their kinetic character [134,135].

Recently, Kalvoda and Budnikov [84,85] have shown that, under the conditions of oscillographic polarography, benzamide is reduced at negative potentials, whereas it is polarographically inactive. This reduction can be observed clearly by recording oscillograms with two dropping electrodes. The $dE/dt = f(E)$ curves for acidic solutions of pH < 2.5 show two kinetic incisions, which disappear when gelatin is added. During the reduction of benzamide in acidic solutions, the amino-alcohol is first formed:



This amino-alcohol is unstable in acid solutions and decomposes:



The benzylideneimine is also unstable in acid solutions, and decomposes to form benzaldehyde. The two incisions on the $dE/dt = f(E)$ curves correspond exactly to the reduction of benzaldehyde and its imine. With rise in the temperature of the solution and increase in the acid concentration, the incision for benzaldehyde becomes deeper, indicating an increase in the rate of decomposition of the imine and confirming the above reaction scheme. Behaviour analogous to that of benzamide is shown by nicotinamide, except that the oscillopolarogram for an acid solution of nicotinamide contains one incision corresponding to formylpyridine. The above scheme for the reduction of benzamide is applicable not only to oscillopolarographic conditions but also to the conditions of ordinary preparative electrolysis with controlled current, and is consistent with published data.

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The above factual material shows clearly the possible applications of oscillographic polarography in the study of organic compounds. Oscillographic polarography, however, is not a universal method of study, and it would be wrong to regard it as competing with classical polarography. The two methods rather supplement one another.

In order to use the advantages given by a combination of the two methods, it is necessary to known their possibilities for solving problems in organic chemistry. The possibilities of classical polarography have been discussed many times [136–139].

The above material shows that the advantages of oscillographic polarography are that it makes possible the study of phenomena which cannot be studied by ordinary polarographic methods, *e.g.* the formation of artefacts, and the analysis of a number of compounds which are considered inactive in classical polarography; it also makes it possible to obtain information much more rapidly.

Moreover, oscillographic polarography has much higher sensitivity and resolving power than the polarographic method. In classical polarography two waves can be observed separately if their potentials differ by not less than 200 mV, whereas in oscillography the difference in the potentials of the incisions or peaks which can be clearly distinguished should be about 100 mV, and in the case of the derivative curves ~ 40 mV. The method of oscillographic polarography with partial differentiation, developed by Nigmatullin and coworkers [140], has even greater resolving power and may in future play an important part in the study of organic compounds with similar structures.

There are other limitations at present on the use of oscillographic polarography for the solution of theoretical problems. In the first place, to obtain quantitative results it is necessary to take into account the state of the depolariser at the electrode surface, but this is not always possible because of the repeated a.c. polarisation. Even in the case of single-period oscillograms ("first curves") it is difficult to make allowance for this factor, since the form of the curve is influenced by the d.c. component, whose magnitude is often disregarded.

The theory of the oscillographic curves also takes into account several factors influencing the results obtained. Oscillographic polarography does not yet, however, exhibit the same definite correlations and simplicity characteristic of classical polarography. Neither fluctuations in current influencing the drop time of the mercury, nor periodic changes in the electrode surface leading to its vibration, complicate the overall picture of the electrode process in ordinary polarography.

The results obtained by the oscillographic method in most cases describe the electrode process to a first approximation, and at present there is, unfortunately, no case where oscillographic polarography has been used for the

quantitative study of the mechanism of electrochemical reactions. In the case of the $dE/dt = f(E)$ curves, the depth of the incision is not directly proportional to the concentration of depolariser. This undoubtedly complicates the quantitative application of the oscillographic dE/dt method. The mutual influence of different depolarisers, present together in solution, on the shape of the incisions on the oscillogram also makes quantitative calculations difficult. Finally, the accuracy and the reproducibility of the oscillographic curves are as yet inadequate for quantitative theoretical studies, whereas this cannot be said of classical polarography. At the present time, oscillographic polarography is in the state in which classical polarography found itself in the 1930's. The number of compounds which have been studied by this method is also still small.

Oscillographic polarography is now developing rapidly. Basic factual material obtained by the oscillographic method is being extended. The results of studies should, however, be treated and presented in a fashion appropriate to the present state of physical and chemical knowledge. It is quite insufficient to restrict the presentation to a description of the experimental data. Conditions now permit a direct approach to the study of electrochemical processes by oscillographic polarography. The task now facing oscillographic polarography is to study the nature and the reasons for the appearance of incisions or peaks on oscillograms, and by means of them to provide a fairly complete characterisation of the electrochemical process [8,140].

To permit comparison of results obtained by oscillographic and classical polarography, it is necessary to use polarisation at low frequencies (single-period curves). The interpretation of oscillographic curves is greatly facilitated by the use of a polarographic method in which an a.c. voltage of constant and fairly low amplitude is applied together with a d.c. polarising voltage. In a number of cases good agreement has been observed between results obtained by this method and by the dE/dt method for surface-active compounds (various alcohols, narcotine, atropine, tryptophan, etc.). To interpret the oscillograms, it is also necessary to use ordinary polarography with a Kalousek switch, and polarography at a stationary mercury electrode. The use of oscillographic polarography to prove the formation of intermediate products in the electrochemical synthesis of organic compounds is also extremely promising. Recently, oscillographic polarography has been used successfully to study complex biochemical materials (amino-acids, steroids, alkaloids, etc.). Attempts to produce an atlas of oscillograms for the identification of organic compounds are of interest in this connection, since in some cases even the shape of the curve may be of assistance in analysis.

The present review has not dealt with the possibilities of each method of oscillographic polarography, and it has not examined the advantages of methods involving the use of sinusoidal and sawtoothed or triangular voltages applied to the polarographic cell. It has also neglected problems associated with the use of methods in which $i = f(t)$, $E = f(t)$, and $dE/dt = f(E)$ curves are studied.

A combination of these methods will undoubtedly extend considerably our ideas regarding the nature of electrochemical processes involving organic compounds.

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ADVANCES IN THE SYNTHESIS OF THERMOSTABLE POLYMERS

V. V. Korshak and E. S. Krongauz

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I. INTRODUCTION

Great interest has recently been shown in thermostable polymers. This has arisen from the needs of aviation, radio engineering, rocket technology, and other fields which demand the use of increasingly thermostable materials.

Polymers employed in electrical insulation and as working parts in various machines and equipment must operate at high temperatures for a long time and still maintain their mechanical properties. However, the prolonged action of a high temperature has a harmful effect on polymers, causing them to break down both by the direct action of temperature and by the rapid occurrence at elevated temperatures of chemical reactions with oxygen, water, and other chemical reagents.

It must first be noted that the actual concept of thermal stability is quite indefinite, so that different authors frequently use the term in different senses. We shall define thermal stability by the temperature at which polymers still retain their shape and their characteristic set of mechanical properties. In a definite sense thermal stability corresponds to the melting point or softening point of the polymers.

The mechanical strength of polymers varies with temperature as shown in Fig. 1. Thus the thermal stability at zero load will correspond to the softening point of the polymer. The greater the load the lower must be the temperature at which the polymer would retain the required strength. In order to specify the thermal stability of a polymer completely, therefore, the load at which it has been determined must be known. Consequently there must be a direct link between the thermal stability, conceived as the limiting temperature at which the polymer still withstands a given load, and the softening point of the polymer, which relation can in general be expressed by the formula $\tau = bt_{sft}$, where τ is the thermal stability (°C), t_{sft} the softening point (°C), and $b = 1 - \sigma_\tau/\sigma_0$, in which σ_τ and σ_0 are the loads (kg cm^{-2}) at the respective temperatures τ and 0°.

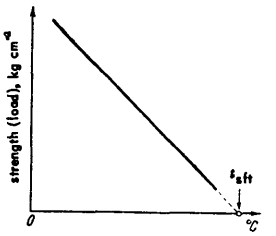


Fig. 1. Temperature dependence of strength of polymer.

A similar formula was proposed by Ratner *et al.*[8], who considered various aspects of its application in detail. These workers describe different methods of testing and estimating the thermal stability of polymers.

Thermal stability is also very widely taken to mean the ability of a polymer to maintain unchanged its engineering properties and structure at high temperatures. It depends on the strength of the bonds between atoms in the polymer molecule and the readiness with which the molecule undergoes various reactions, primarily those involving degradation.

Polymers are specified also by such concepts as heat--resistance or deformation temperature, which are defined with respect to special standards. A very convenient characteristic for comparing the operational properties of polymers may be the temperature at which 50% of their initial strength is lost.

Interest in this important branch of polymer chemistry is continually increasing, as is shown in the numerous papers, reviews, and monographs which have been published[1-10]. Our aim in the present review is to examine and summarise information published recently on the dependence of the thermal stability of polymers on their structure, and on this basis to give an overall picture of the present state of the problem.

II. DEPENDENCE OF THERMAL STABILITY ON STRUCTURE OF MONOMER UNIT

Examination of the dependence of thermal stability on the structure of the macromolecule is one of the most important aspects of the broad problem of studying the relation between the structure of a polymer and its properties. From this point of view both the structure of the monomer unit and that of the macromolecule as a whole are significant, as is also the interaction between the polymer molecules, which determines the structure of the polymer comprising these macromolecules. We shall therefore describe separately the effects which may be attributed to the structures of the monomer unit, the macromolecule, and finally the polymer as a whole, paying special attention to the behaviour of the polymer at high temperatures.

The structure of the monomer unit is the most important factor determining the melting point of a polymer. Fig. 2 illustrates the temperature ranges within which lie the melting points of polymers of various classes. It clearly shows differences between each type of polymer. Melting points below 0° are found only in the polymeric vinyl ethers, hetero-chain polyesters, and polysiloxanes. The higher we rise on the temperature scale, the fewer polymers we find remaining on the diagram. The majority of polymers melt below 200°, and only such groups as polyphenylenes, polyarylates, polybenzimidazoles, some polysiloxanes, polychelates, polypyromellitimides, and polypyrazoles include members which melt above 300°. In nearly all these cases the monomer unit contains a ring: *i.e.* they are cyclo-chain polymers. The presence of various rings in the macromolecular chain in such polymers confers on it great rigidity, and results in strong intermolecular forces, which are responsible for the high melting point.

In contrast to the above cyclo-chain polymers, ordinary straight-chain polymers, exemplified in the many poly-

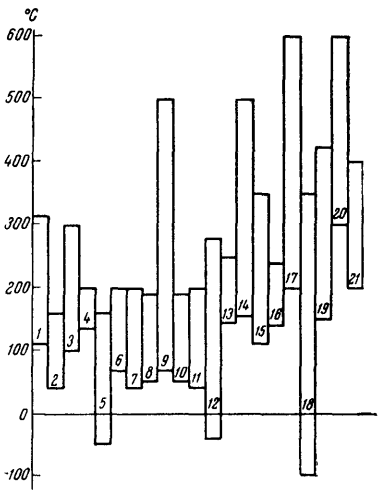


Fig. 2. Temperature ranges of melting points (softening points) for various classes of polymers:
1) polymeric hydrocarbons; 2) polymeric chlorinated derivatives; 3) polymeric fluorinated derivatives; 4) polymeric alcohols; 5) polymeric vinyl ethers; 6) polymeric vinyl esters; 7) polymeric acrylic esters; 8) polymeric dienes; 9) polyphenylenes; 10) polyethers; 11) polyacetals; 12) polyesters; 13) polycarbonates; 14) polyarylates; 15) polyamides; 16) polyerethanes; 17) polybenzimidazoles; 18) polysiloxanes; 19) polychelates; 20) polypyromellitimides; 21) polypyrazoles.

vinyl compounds, comprise monomer units consisting solely of individual carbon atoms extending in a linear chain $-CH_2-CHX-$. The great flexibility of such a chain and the weak intermolecular forces are responsible for the lower melting points of these and similar polymers.

The melting (softening) points of vinyl polymers depend on the number and nature of the substituents in the monomer unit, as well as on the structure of the chain itself (on stereoregularity, cross-linking, etc.), which will be considered in greater detail below.

The length of the monomer unit, the nature of the atoms it contains, and also the possibility of hydrogen bonding have a significant influence. Thus it has long been established with polyamides and polyesters that polymers in which the monomer unit contains an even number of methylene groups melt at higher temperatures than analogous compounds containing an odd number of atoms in the unit. Figs. 3 and 4 show the variation in the melting points[11] of polyesters of ethylene glycol and of eicosamethylene glycol with dicarboxylic acids containing even and odd numbers of methylene groups in the monomer unit. A similar pattern is observed with polyamides (Fig. 5).[12]

Replacement of a methylene group by an oxygen atom results at first in a rise in melting point, as is readily seen on comparing polyethylene with polyformaldehyde (m.p. 115° and 185° respectively). With a longer monomer unit, however, the melting points of both polyethers and polyesters fall. This is shown especially clearly by the polyesters of triethylene glycol, which melt below 0° (Fig. 6).[13]

In contrast, introduction of an amide grouping NHCO into a polymer chain produces a marked rise in the melting

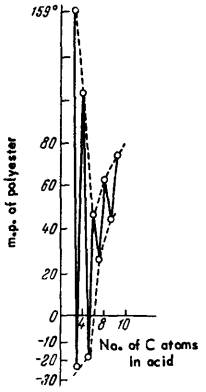


Fig. 3. Variation in melting point of polyesters of ethylene glycol.

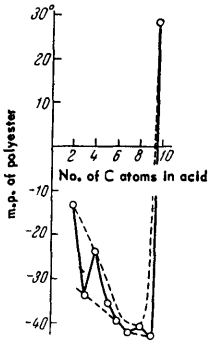


Fig. 6. Variation in melting point of polyesters of triethylene glycol.

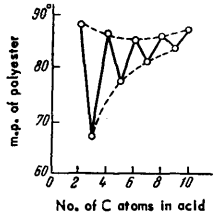


Fig. 4. Variation in melting point of polyesters of eicosamethylene glycol.

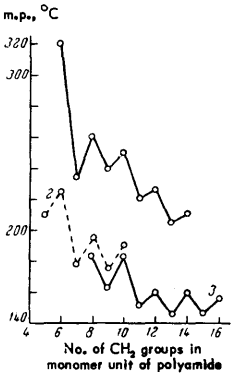


Fig. 5. Variation in melting point of polyamides of differing structure with number of methylene groups in molecules of the initial monomers:
1) polyamides from hexamethylenediamine and various dicarboxylic acids;
2) polyamides from ω-amino-acids;
3) polyamides from tetramethylene glycol and various diisocyanates.

points of the resulting polyamides, probably associated with a strengthening of the forces between the macromolecules.

The effect of substitution in the chain, as well as the general relationship between the melting points of hetero-chain polymers and their chain structure, may be traced by comparing hetero-chain polymers containing different hetero-atoms in the macromolecule.

Korshak and Frunze showed [14,15] that a quite definite relationship exists between the melting points of polyamides and the chemical structure of the monomer unit. In the case of aliphatic polyamides these relations are so simple that they can be expressed by an empirical linear equation linking melting point with the hetero-chain parameter of the polyamides: $Y = aX + b$, where Y is the melting point of the polyamide, X the parameter, representing the ratio, expressed as a percentage, of the number of groups containing hetero-atoms to the number of methylene groups, while a and b are constants characteristic of each series of polyamides.

The above workers proposed regarding polyamides in this respect as copolymers of polyethylene and isocyanic acid HNCO, and showed that the relative arrangement of these components had no effect on the melting point of the polymers, which depended solely on the ratio $CONH/CH_2CH_2$, *i.e.* on the molecular percentage of amide groups in the polymer.

It was shown that this applied to other series of hetero-chain polymers — polyureas, polyurethanes, polyesters, polyanhydrides, etc. — as well as to polyamides (Table 1). In all these series a linear relation was found, illustrated graphically in Fig. 7. The melting-point graphs intersect at a point corresponding to the melting point of polyethylene, *i.e.* to zero content of amide or other groups.

As we shall show later, all the relationships become more complicated on introduction into the polymer chain of aromatic or hydroaromatic rings, hetero-atoms, or side-chains. Replacement of methylene hydrogen atoms by other atoms or groups has a great effect on the melting point of the polymer, both the nature of the substituents and their number and relative arrangement in the chain and in space being of great significance.

Introduction of one substituent into each monomer unit of an atactic polymer in most cases lowers the melting

TABLE 1. Equations relating melting point with the hetero-chain parameter of various groups of polymers[14,15].

Polymer group	Equation
Polyureas with an even number of methylene groups in the monomer unit	$Y = 8.4X + 110$
Polyamides with an even number of methylene groups in the unit	$Y = 7X + 110$
Polyamides as above, from other data	$Y = 7X + 125$
Polyamides from dicarboxylic acids with odd, and diamines with even, numbers of methylene groups	$Y = 6.2X + 110$
Polyamides from even dicarboxylic acids and odd diamines	$Y = 5.6X + 110$
Polyamides from odd dicarboxylic acids and odd diamines	$Y = 4.5X + 110$
Polyurethanes with an even number of methylene groups in the monomer unit	$Y = 3.5X + 110$
Polyamides with sulphide sulphur in the chain	$Y = 3X + 110$
Polyamides with ethereal oxygen in the chain	$Y = 1.9X + 110$
Polyanhydrides with an even number of methylene groups in the unit	$Y = -2.5X + 110$
Polyesters with an even number of methylene groups in the unit	$Y = -3X + 110$
Polyesters with an odd number of methylene groups in the unit	$Y = -3.6X + 110$
Polyanhydrides with an odd number of methylene groups	$Y = -3.6X + 110$

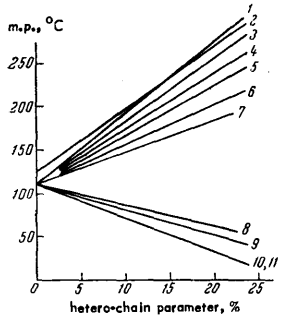


Fig. 7. Dependence of melting point on hetero-chain parameter for:
1) polyureas; 2) polyamides with an even number of CH_2 groups in the diamine and in the acid;
3) polyamides as (2), from measurements of the true thermodynamic melting points; 4) polyamides from even diamines and odd acids;
5) polyamides from odd diamines and even acids;
6) polyamides from odd diamines and odd acids;
7) polyurethanes; 8) polyanhydrides with an even number of CH_2 groups in the monomer unit;
9) polyesters from even glycols and even acids;
10) polyesters from odd acids and odd glycols;
11) polyanhydrides with an odd number of CH_2 groups.

point. Thus polyethylene melts at a higher temperature than poly(vinyl chloride), poly(vinyl acetate), and polystyrene, as is seen from Table 2.

We thus see that in most cases, with the exception of poly(vinyl fluoride), introduction of one substituent into the monomer unit of polyethylene lowers the softening temperature. However, a different situation is found with stereoregular polymers, which usually melt at higher temperatures than does polyethylene, as will be discussed in greater detail below.

In just the same way the presence of substituents in the molecules of polyamides, polyesters, and other polymers results in lower melting (softening) points, as is evident in

TABLE 2. Melting or softening points of polymers of type CH_2–CHX.

Polymer	Melting or softening point, °C
Polyethylene	115
Poly(vinyl chloride)	80
Poly(vinyl fluoride)	200
Poly(vinyl acetate)	70
Polystyrene	90
Polypropylene	80

the case of the polyesters of propylene glycol with various dicarboxylic acids[13]. These polyesters melt below 0°, as is shown in Fig. 8.

Introduction of two substituents may produce either a rise or a fall in the melting point of the polymers (Table 3).

The polymer chain can be made rigid, and free rotation about single bonds hindered, by introducing various atoms and groups into the macromolecule. Thus polytetrafluoroethylene melts at 330°, in contrast to polyethylene (m.p. 115°), although the forces of intermolecular interaction are almost the same in these two polymers. The potential barrier preventing free rotation about C–C bonds was found to be far higher in hexafluoroethane than in ethane itself (4550 and 3000 cal respectively). If it is assumed that similar potential barriers remain in the polymers, these concepts can be used, according to Billmeyer[16], to explain the high melting points of fluorinated polymers as a result of greater rigidity of the polymer chain caused by the screening effect of the densely packed fluorine atoms.

The higher melting points of polymers obtained from branched α-alkenes compared with those of linear α-alkenes

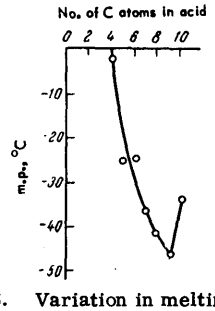


Fig. 8. Variation in melting point of polyesters of propylene glycol.

TABLE 3. Melting points of polymers of type CH_2–CX_2.

Polymer	Melting or softening point, °C
Poly(vinylidene chloride)	185
Poly(vinylidene fluoride)	170
Poly(methyl methacrylate)	125
Poly-α-methylstyrene	160
Polymethacrylonitrile	115

can also be explained by the increased rigidity of the polymer chain produced by the introduction of substituents, whose presence hinders free rotation about the carbon–carbon bonds. In the case of atactic polymers, the increase in rigidity of the polymer chain accompanying introduction of substituents is usually balanced by a decrease in interchain interaction caused by the accompanying breakdown in molecular symmetry and in dense packing.

Cyclo-chain polymers containing carbocyclic or heterocyclic rings in the chain are usually distinguished by high thermal stability. Table 4 gives melting (softening) points for series of cyclo-chain polymers, and includes for comparison melting points of structurally analogous polymers not containing rings. The introduction of *p*-phenylene groups into a polymer chain always results in a rise in melting point (see Table 4).

An increase in cohesive forces also cannot explain the improved thermal stability of the polymers in this case, since the increment in the energy of these forces for a phenyl group is almost the same as for six methylene groups (determined by comparing melting points and latent heats of vaporisation of aromatic and aliphatic compounds containing the same number of carbon atoms). Moreover, the crystal structure of poly(ethylene terephthalate) indicates that the distances between atoms of neighbouring macromolecules are the usual van der Waals distances. The considerable rise in melting point of polymers produced by introducing an aromatic ring into the chain must be due to the rigidity of the chain, and probably associated also with conjugation.

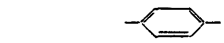
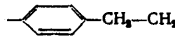
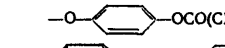
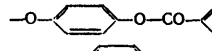
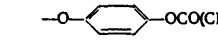
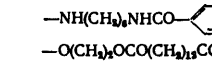
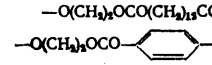
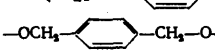
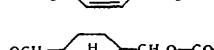
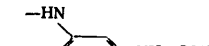
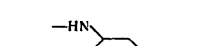
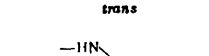
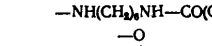
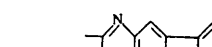
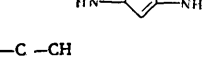
The effect of aromatic rings in a chain on the thermal stability of polymers can be seen especially clearly in a novel class of polymers, the polyarylates. Comparison of the softening temperatures of polyarylates of adipic acid with those of the corresponding polyarylates of terephthalic acid, which have been synthesised and investigated by Korshak and Vinogradova [10], has shown that replacement of aliphatic by aromatic (terephthalic) acid residues in the polyester chain raises considerably the softening point of the polyarylates. For example, the softening point of the polyarylate of quinol with adipic acid is 225°, whereas poly(quinol terephthalate) does not melt below 500° (Table 4). Polyarylates of adipic acid possess higher softening points than do the corresponding polyarylates of sebacic acid, probably owing to the diminished rigidity of the polymer chains in the latter case, resulting from the lower concentration of aromatic rings.

Introduction of 1,5-naphthylene and *pp'*-biphenylylene groups into the polymer chain also produces a rise in melting point compared with the corresponding polymers containing only one benzene ring (Table 4).

It is interesting that hydrogenated aromatic rings also raise the melting point, sometimes to a greater extent than do aromatic rings, as can be seen from Table 4. Various heterocycles are also extremely effective, their introduction into the macromolecule greatly raising the melting point of the polymers (Table 4), which include polybenzimidazoles, polypyrazoles, polypyromellitimides, etc.

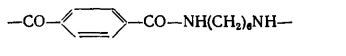
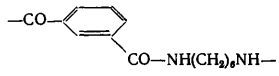
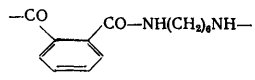
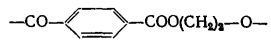
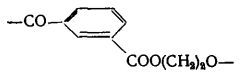
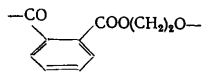
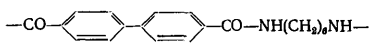
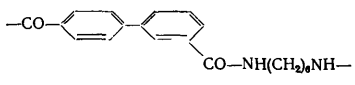
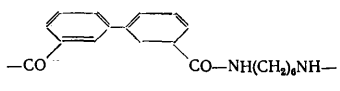
The examples which have been cited show that *para*-substituted rings very greatly raise the melting points of polymers. Rings which are substituted in *ortho* and *meta* positions have quite different effects. Their presence usually results in lower melting points, as is seen from the examples in Table 5, and it also diminishes the crystallinity.

TABLE 4. Effect of the presence of rings in the chain on the melting points of polymers.

Monomer unit	Melting or softening point, °C	Ref.
$-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-$	115	17
	530	18
	380	19
$-O(CH_2)_2OCO(CH_2)_6CO-$	45	20
	264	21
	225	22
	500	23
	172	22
$-NH(CH_2)_6NHCO(CH_2)_6CO-$	235	23
	350 (decomp.)	11
$-O(CH_2)_2OCO(CH_2)_{12}CO-$	80	23
	330	11
	238	24
	290	25
	258	11
 *trans*	300	26
 *cis*	165	26
$-NH(CH_2)_6NH-CO(CH_2)_4CO-$	250	26
	630 (decomp.)	27
	600	28
	500	28
	280	29
	400	30,31

Korshak and Vinogradova [23] showed that the softening temperature of a polyarylate depends on the relative arrangement of functional groups both in the acid and in the diol. Polyesters of acids and diols having their functional groups in the *para* positions have higher softening

TABLE 5. Effect of substitution isomerism in the ring on the melting points of polymers.

Monomer unit	Melting & softening point, °C	Ref.
	350	11
	150	11
	50	11
	256	11
	103	11
	63	11
	360	11
	140	11
	142	11

points than polyesters of initial components with *meta*--oriented functional groups. Thus polyarylates formed by resorcinol with terephthalic and isophthalic acids soften considerably below the corresponding polyarylates of quinol; the polyarylates of these acids with 2,2-diphenylpropane-*pp'*-diol, hexaphenylxylene-*pp'*-diol, and naphthalenediols also support this generalisation[23,27,32].

The energy of free rotation, or the energy required to surmount the potential barrier opposing rotation, is about 1–5 kcal mole^{-1}, which is of the same order as the energy of cohesion. Potential barriers to rotation about single C–C bonds adjacent to a double C=C bond are lower than in saturated molecules[33,34]. Thus introduction of double bonds into a polymer molecule increases its flexibility, which is shown in a lowering of the softening point of the polymer. On the other hand, the presence of conjugated double and triple bonds makes the molecule rigid and raises the softening point[35]. Thus "carbyne",[36] which is a linear polymer with a system of conjugated triple bonds $(C{\equiv}C)_x$, is unchanged by temperatures up to 2300°. Polyvinylene[37] $(CH{=}CH)_x$, obtained by the dehydrogenation of poly(vinyl alcohol), is unchanged by heating up to 800°.

The strength of the bonds between atoms in the monomer unit is of great significance for the thermal stability of polymers. Table 6 gives data on the stabilities of bonds between individual elements. Elements whose bonding energy exceeds 37 kcal mole^{-1} are able to form polymers. With lower values formation of homo-chain polymers is not observed, as is evident from the example of nitrogen and

TABLE 6. Energy of bonds between like atoms[38].

Bond	Bond energy, kcal mole^{-1}	Bond	Bond energy, kcal mole^{-1}
C—C	80.0	Sb—Sb	42.0
S—S	63.0	Ge—Ge	39.2
P—P	53.0	As—As	39.0
Se—Se	50.0	N—N	37.0
Te—Te	49.0	O—O	34.0
Si—Si	45.0		

oxygen. This capacity is most clearly developed with carbon, which is distinguished by the highest bonding energy.

A very different situation is found with hetero-chain polymers, and the number of elements capable of forming them is much greater. Table 7 gives bond energies which are typical of hetero-chain polymers. It is seen that these values are quite considerable, and in many cases exceed the bond energies of homo-chain polymers. In most cases, therefore, hetero-chain polymers are hard, durable substances of high melting point.

From a study of polymers having inorganic chains Andrianov[39] concluded that an **E–E'** bond will be more stable with less ionic character in the bonds forming the main chain, *i.e.* the closer the mean electronegativity of the two elements forming the bond to the electronegativity of the carbon atom, which is 2.5. Table 8 gives electronegativity values for several elements.

Andrianov points out[39] that examples of organoelementary polymers having this structure are provided by the polyorganosiloxanes and the polyaluminoorganosiloxanes, whose chains are built up from alternating electropositive silicon and aluminium atoms and electronegative oxygen atoms, the mean electronegativity of the bond between these two elements approaching that of carbon. These chains reproduce the skeleton of the inorganic polymers — quartz and aluminosilicates — occurring in Nature; they are stable to heat and hydrolysis.

TABLE 7. Energy of bonds between unlike atoms[38].

Bond	Bond energy, kcal mole^{-1}	Bond	Bond energy, kcal mole^{-1}
B—O	119.3	C—N	66.0
B—N	104.3	As—O	64.5
Si—O	89.3	Al—C	61.6
B—C	89.0	C—S	61.5
P^{III}—O	81.7	Si—S	60.9
C—O	79.0	C—Si	57.6

TABLE 8. Electronegativities of elements in Groups III–VI of the Periodic System[39].

III	IV	V	VI
B —2.0	C —2.5	N —3.0	O —3.5
Al—1.5	Si —1.8	P —2.1	S —2.5
	Ge—1.8	As—2.0	Se—2.4
	Ti—1.6	V —1.9	Te—2.1
	Sn—1.7	Sb—2.1	Mo—2.1
	Zr—1.5		W —2.0
	Pb—1.6		

The stability of the bonds between substituents and main chain is also of great significance. Thus poly(vinyl chloride) is a polymer of relatively low thermal stability, since it readily eliminates hydrogen chloride. The same applies to poly(vinylidene chloride), poly(vinyl alcohol), and compounds of similar structure. These considerations apply also to the side-chains. Thus the higher thermal stability of Penton (a polymer of 3,3-bischloromethyloxetan) is explained by the fact that the carbon atom adjacent to the chloromethyl group carries no hydrogen atom, which would be necessary for the formation of hydrogen chloride.

The results considered above make clear the relationship which can be detected between the structure of the monomer unit and the properties of the polymer. However, this does not exhaust the problem of the link between thermal stability and polymer structure. Other factors also have a great influence, and will be considered later. These are the structure of the macromolecule itself and the various changes it undergoes at elevated temperatures.

III. DEPENDENCE OF THERMAL STABILITY ON STRUCTURE OF POLYMER CHAIN

Several structural features of the macromolecule are as important as the structure of the monomer unit, among them being the regularity of the chain, the presence of branching or cross-links between chains, the ability to crystallise, the strength of the intermolecular forces, and the flexibility of the macromolecule.

A regular alternation of monomer units in the macromolecule is a factor tending to raise the melting point. This is shown especially clearly when homopolymers are compared with copolymers: the latter always have lower melting points, since the disordered arrangement of monomer units impedes crystallisation and any ordering of the macromolecular chains in the mass of the polymer in general. Thus polyamides having a regular arrangement of monomer units, prepared by migration copolymerisation from bisoxazolones and diamines, have higher melting points than polyamides of similar composition but with a disordered arrangement of monomer units, obtained by polycondensation of the starting materials[40].

A still greater effect in raising melting point is obtained by stereoregular arrangement of the units in a chain, which ensures not only the accurate alternation of monomer units but also their regular spatial arrangement, as we observe in the case of stereoregular (isotactic and syndiotactic) polymers.

Table 9 gives examples of compounds of stereoregular and atactic structure which have high melting points. They illustrate well the considerable rise in melting point in stereoregular as compared with atactic polymers of the same composition. The former are crystalline even in the presence of bulky substituents, which do not interfere with crystallisation, in contrast to amorphous atactic polymers, in which the ability to crystallise is often completely absent owing to steric hindrance by the substituents. Crystallinity is an important factor tending to increase thermal stability. This question has been discussed in detail in the literature[41].

The presence of branching impedes crystallisation and ordering of the macromolecule. The classical example of this is polyethylene produced at high pressures, which melts at 105°, whereas low-pressure polyethylene melts

TABLE 9. Examples of high-melting stereoregular polymers.

Polymer	Melting or softening point, °C		Ref.
	cryst.	amorphous	
Poly-3,3-dimethylbut-1-ene	370	—	41
Poly-4,4-dimethylpent-1-ene	320	—	41
Poly-4,4-dimethylhex-1-ene	350	—	41
Poly-3-phenylbut-1-ene	360	—	41
Poly-o-methylstyrene	360	120	41
Poly-2,4-dimethylstyrene	310	180	41
Poly-2,5-dimethylstyrene	330	170	41
Poly-1-vinylnaphthalene	350	100	41
Polyvinylcyclohexane	300	—	41
Polyallyldimethylphenylsilane	300	—	42
Polydiallylmethylphenylsilane	400	—	42

at 138°.[17] The structural difference between them is that the former contains branched macromolecules, and the latter unbranched macromolecules. A fair number of examples of this kind are now known. It can probably be accepted as proved that the lower melting points of polymers obtained by radical polymerisation are due not only to their atactic structure but also to their inherently branched character.

Cross-linked polymers have higher thermal stability. The formation of bridges between chains increases not only the thermal stability of the polymers but also the modulus of elasticity and the hardness, while diminishing the elongation at break. Table 10 gives the effect of the number of cross-links, formed on copolymerisation of styrene with divinylbenzene, on the glass temperature of the polymer[43].

Later work showed that the thermal stability of copolymers of styrene and *p*-divinylbenzene increases linearly at a rate approximately equivalent to 3.3 deg per 1% of divinylbenzene. Tensile strength and impact resistance increase with the first 5% of divinylbenzene, and then fall; hardness increases in proportion to the increase in concentration of divinylbenzene[44]. According to Rutovskii and Shur[45] the thermal stability of poly(methyl methacrylate) can be improved by copolymerisation with allyl methacrylate (Table 11).

TABLE 10. Glass points of styrene–divinylbenzene copolymers.

Divinylbenzene content	Glass point, °C
0	87.0
0.6	89.5
1.5	97.0

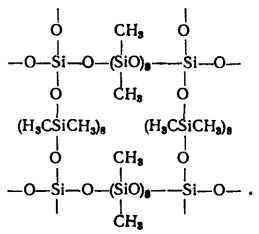
TABLE 11. Thermal stability of copolymers of the meacrylate and allyl meacrylate.

Allyl methacrylate content, %	Thermal stability according to Wieck, °C
0	116
10	141

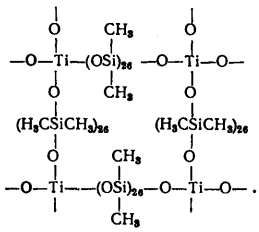
Recently Korshak and Vinogradova have established that the cross-linking of linear saturated polyarylates with formaldehyde and a novolak increases their thermal stability. Polyarylates obtained from isophthalic or terephthalic acid with 2,2-diphenylpropane-*pp'*-diol or phenolphthalein and *o*-allylphenol or the diallyl derivative of the diol readily underwent further hardening, both thermally and by copolymerisation with methyl methacrylate. The strengthened polyarylates are characterised by rubberlike elastic deformation over a wide range, and break down appreciably only at temperatures above 500°.[46-48]

A case of the improvement of the mechanical properties and thermal stability of polymers which has been known for a long time is the vulcanisation of rubber and other polymers by means of sulphur or a peroxide. Recently ionising radiation, has been successfully used for this purpose. Thus the γ irradiation of polyethylene increases its thermal stability to 250°.[50]

Andrianov and his collaborators[51] have synthesised regular polymers of three-dimensional structure from multifunctional oligomers containing unifunctional groups at the ends of branches, to which he assigns the structure



Condensation of ter- and quadri-functional oligomers also yields polyorganosiloxanes, as well as organoelementary siloxane polymers, of regular structure



The physical properties of polymers, such as softening and melting points, tendency to crystallisation, solubility, mechanical characteristics, etc., are directly linked with the structure of the polymer chain, being determined mainly by the stereochemical regularity of the macromolecule, its flexibility, and also the intermolecular forces. Interaction between polymeric molecules is responsible for the mechanical strength of the polymer and its thermal stability.

The intermolecular forces determining the thermal stability of polymers include dipole interaction, inductive forces, dispersion forces, and hydrogen bonds. Apart from dispersion forces, they all depend on temperature, becoming weaker as it rises. Intermolecular forces are of great significance, their strength determining to a considerable extent the limiting temperature which the polymer will withstand without breaking down.

The forces acting between molecules are electrical in nature. Non-polar molecules exhibit instantaneous dipoles, caused by the motion of electrons. Although the mean value of these dipole moments is zero, they are nevertheless able to polarise neighbouring molecules, inducing in them corresponding instantaneous dipoles. These interactions produce intermolecular forces of attraction, the so-called "dispersion forces". According to London[52] the potential energy of two identical molecules can be calculated from the formula

$$E = -\frac{3\alpha^2 I}{4r^6},$$

where E is the potential energy, α the polarisability, r the distance between the molecules, and I the ionisation potential.

In the presence of a permanent dipole, the molecule can polarise neighbouring molecules, producing additional forces of attraction, inductive forces. In this case the potential energy will be

$$E = \frac{2\alpha\mu^2}{r^6},$$

where μ is the permanent dipole moment.

The mutual orientation of two dipoles is responsible for larger forces of attraction between the molecules. The mean value taken over all directions gives the increase in potential energy due to orientation forces calculated by means of the equation

$$E = \frac{2\mu^4}{3r^6RT}.$$

Walker[53] notes the following two important points about the above three expressions: (1) dispersion forces are independent of temperature, while depending on the number and strength of bonding of electrons, especially valency electrons; and (2) orientation forces are inversely proportional to the absolute temperature.

Since orientation forces vary with μ^4, their magnitude in polymers containing polar substituents should substantially affect the density of cohesive energy.

Intermolecular forces may be diminished in the case of a chemical structure which prevents the approach of certain atoms and groups to the corresponding atoms or groups in other molecules. Dispersion and orientation forces are inversely proportional to the sixth power of the distance, and therefore the energy of interaction of atoms or groups which are screened by inert groups is significantly lower.

Hydrogen bonds represent a special case of dipole interaction, in which the negative and the positive charge are arranged in such a way that the dipoles can approach very close together, which results in an increase in their energy of interaction.

Thus the stronger the forces of interchain interaction the greater the energy which must be supplied to destroy the order present in the polymer. It follows from the above that the magnitude of these intermolecular forces depends both on "specific" forces of attraction acting between groups in the polymer and on the geometry of the polymer molecules. A convenient measure of intermolecular interaction is the energy of cohesion of individual segments or structural units, calculated on the basis of an additive scheme in which a definite increment of cohesion energy is assigned to each chemical group of atoms.

Bunn[54] used these data to calculate cohesion energies for polymers (Table 12). In order to obtain greater clarity and to make it easier to compare forces of interaction between various groups, Mark[55] made calculations of molecular cohesion for a chain segment 5 Å long (Table 13).

Thus the energy of intermolecular interaction in various polymers (1–6 kcal mole^{-1}) is insignificant in comparison with the energy of a homopolar bond in the main chain (rupture of a single C–C bond requires energy of around 70–100 kcal mole^{-1}). At high degrees of polymerisation, however, the total energy of intermolecular interaction may exceed the energy of the valency bonds in the main chain, and then degradation will involve intramolecular cleavage at valency bonds. The data in Table 12 show that the specific cohesive force for a saturated hydrocarbon chain is small, whereas the presence of polar groups increases it. Simple hydrocarbon polymers, such as polyisobutene and natural rubber, are characterised by low values of specific molar cohesive energy, so that they have low softening points and are readily converted into elastic materials. The introduction of polar groups usually raises the softening point of polymers.

The opposite effect — the neutralisation or elimination of the polar influence of groups by the introduction of non-polar substituents into the molecule — can also be observed. For example, in the esterification of polyacrylic acid, containing strongly polar carboxy-groups, a lowering of the softening temperature of the polymers can be observed. The non-polar hydrocarbon chain neutralises the polar groups of the ester, the introduction of branched or cyclic alkyl groups affecting the softening point considerably less than does the presence of straight-chain alkyl groups of the same molecular weight in the macromolecular[54].

However, if the thermal stability of polymers is assessed only on the basis of the molar cohesion, several discrepancies are evident in Table 13: the high value of 3400 cal for the cohesion of poly(hexamethylene adipate) is consistent with its high melting point (264°); on the other hand, the cohesion energy of poly(ethylene terephthalate), with the same melting point, is considerably lower (1900 cal); while poly(ethylene adipate), in which the cohesion energy (1800 cal) is almost the same as in poly(ethylene terephthalate), melts at 50°; polystyrene, whose cohesion exceeds that of anid [probably a Russian polyamide fibre (Ed. of Translation)] (4000 cal), has m.p. 80°; Teflon and polymethylene have almost the same value for the intermolecular interaction, while their melting points differ markedly. Poly(methyl methacrylate) $CH_2.C(CH_3)(COOCH_3)$ and poly(ethyl acrylate) $CH_2.CH(COOC_2H_5)$ have the same composition and hence should possess the same cohesion; nevertheless, their thermal stabilities are different. Gutta-percha and rubber, which have the same chemical composition $CH_2.C(CH_3):CH.CH_2$ and the same cohesion, also differ in thermal stability (60° and 0° respectively), probably as a result of different steric positions of the substituent (*trans* and *cis*).

TABLE 12. Energy of cohesion of polymers.

Group	Molar cohesion energy, kcal mole^{-1}	No. of chain units in monomer unit	Mean energy per monomer unit, kcal mole^{-1}	Melting or softening point, °C
$-CH_2-$	680	1	680	136.5
$-CF_2-$	760	1	760	330
$-CHCl\cdot CH_2-$	3040	2	1520	80
$-CCl_2\cdot CH_2-$	3780	2	1890	200
$-C(CH_3)_2-CH_2-$	2680	2	1290	0
$-(CH_2)_{10}CONH-$	19 380	18	1076	149
$-(CH_2)_4CONH(CH_2)_6NHCO-$	23 800	14	1700	265
$-(CH_2)_8CONH(CH_2)_6NHCO-$	26 520	18	1474	215
$-(CH_2)_n CONH-$	5800+680n	n+2	—	—
$-(CH_2)_4COO(CH_2)_2OCO-$	9880	10	988	52
$-(CH_2)_n COO-$	2900+680n	n+2	—	—
$-C_6H_4COO(CH_2)_2OCO-$	11 060	5	2212	264
$-C_6H_4COO(CH_2)_n OCO-$	9700+680n	n+3	—	—
$-C_6H_4-C_6H_4COO(CH_2)_2OCO-$	14 900	5	2980	346
$-C_6H_4-C_6H_4COO(CH_2)_8OCO-$	17 620	9	1958	214
$-CH_2C_6H_4CH_2COOCH_2C_6H_4CH_2OCO-$	16 320	10	1632	146
$-C_6H_4COO(CH_2)_2OCOC_6H_4O(CH_2)_2O-$	18 320	10	1832	240
$-O(CH_2)_2O-C_6H_4COO(CH_2)_nOCOC_6H_4-$	16 960+680n	n+8	—	—
$-(CH_2)_n OCONH-$	8740+680n	n+3	—	—
$-(CH_2)_n O-$	1000+680n	n+1	—	—
$-(CH_2)_n S-$	2200+680n	n+1	—	—
$-(CH_2)_n S_2-$	4400+680n	n+2	—	—
$-C(CH_3)=CH(CH_2)_2-$	3760	3	1250	*cis* 20 *trans* 6

TABLE 13. Molecular cohesion of groups.

Polymer	Groups responsible for attraction	Cohesion energy per 5 Å of chain, cal	Softening points of polymers, °C
Polymethylene $-CH_2-$	(CH_2)	1300	115—130
Polyisobutene $-CH_2-C(CH_3)_2-$	(CH_2); (CH_2)	1200	<0
Natural rubber $-CH_2-C(CH_3)=CH-CH_2-$	(CH_2); $(CH=CCH_3)$	1300	<0
Polybutadiene $-CH_2-CH=CH-CH_2-$	(CH_2); $(CH=CH)$	1100	—
Polychloroprene $-CH_2-CCl=CH-CH_2-$	(CH_2); $(CH=CCl)$	1600	—
Poly(vinyl chloride) $-CH_2-CHCl$	(CH_2); $(CHCl)$	2500	80—90
Poly(vinylidene chloride) $-CH_2CCl_2-$	(CH_2);(CCl_2)	3500	185—200
Poly(vinyl alcohol) $-CH_2-CH(OH)-$	(CH_2); $(CHOH)$	5100	~100
Poly(vinyl acetate) $-CH_2-CH(OOCH_3)-$	(CH_2); $(COOCH_3)$	3200	—
Poly(hexamethylene adipate) $-NH(CH_2)_6NHCO(CH_2)_4CO-$	(CH_2); $(CONH)$; H	3400	264
Poly(ethylene adipate) $-O(CH_2)_2OCO(CH_2)_4CO-$	(CH_2); (COO)	1800	50
Poly(ethylene terephthalate) $-O(CH_2)_2OCOC_6H_4CO-$	(CH_2); (COO)	1900	264
Polytetrafluoroethylene $-CF_2-CF_2-$	(CF_2)	1600	330
Polystyrene $-CH_2CH(C_6H_5)-$	(CH_2); (C_6H_5)	4000	80
Cellulose —C—O—C—	(OH); (—O—)	6200	—
Acetylcellulose —C—O—C—	$(OOCH_3)$; (—O—)	4800	—
Silk fibroin —C—N—C—	(CHP); (CONH); H	9800	—
Polyacrylonitrile $-CH_2-CH(CN)-$	(CH_2); $(CHCN)$	—	220

Korshak, Vinogradova, and Frunze[11,56,57] established several quantitative regularities linking the thermal stabilities of hetero-chain polyesters and polyamides with the structure of the polymer chain. They calculated mean values of the cohesion energy per monomer unit for polyesters of differing structure, and showed that, in homologous series of hetero-chain polyesters, the melting point depends on the mean cohesion energy of unit chain. Figs. 9 and 10[56,57] indicate that the melting points of polyesters obtained from polymethylenedicarboxylic acids and glycols lie on two curves when plotted against cohesion energy, passing through minima at 900–1200 cal.

The fact that the above relationship is not represented by a single curve, *i.e.* that the same cohesion energy corresponds to different melting points, indicates that interchain interaction is strongly dependent on the packing of the polymer chains. Less compact packing does not provide the conditions for complete development of interchain forces. There is no doubt that the polymer chains of aromatic polyesters are intrinsically less flexible than are aliphatic polyesters. However, interchain interaction is not always fully developed in the former. Good "packability" or, what is the same thing, a good "superposability factor" of the individual elements in the polymer molecules with respect to one another, is important for the occurrence of interchain interaction, since the energy of the molecular forces approach vary inversely as the sixth power of the distance between the molecules[57].

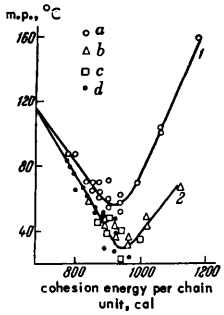


Fig. 9. Variation in melting point of polyesters of polymethylenedicarboxylic acids and glycols with mean cohesion energy per chain unit:
a) both dicarboxylic acids and glycols even; *b*) even acids and odd glycols; *c*) acids and glycols both odd; *d*) odd acids and even glycols.

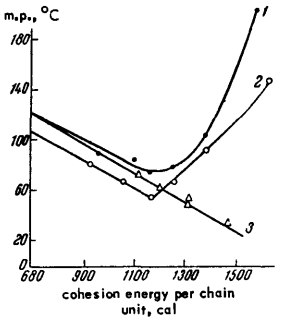


Fig. 10. Variation in melting point of polyesters with mean cohesion energy of chain unit:
1) *p*-xylylene glycol and even polymethylenedicarboxylic acids; 2) benzene-*p*-diacetic acid and even polymethylene glycols; 3) *p*-xylylene glycol and benzene-*p*-diacetic acid, polyesters containing an odd number of methylene groups in the repeating unit.

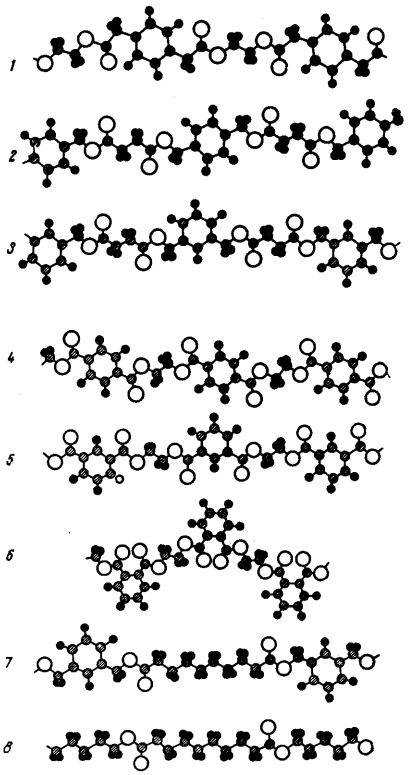


Fig. 11. Diagrammatic view of polymer chains in polyesters:
1) of benzene-*p*-diacetic acid with ethylene glycol; 2) of *p*-xylylene glycol with succinic acid; 3) of *m*-xylylene glycol with succinic acid; 4) poly(ethylene terephthalate); 5) poly(ethylene isophthalate); 6) poly(ethylene phthalate); 7) poly-(*m*-xylylene succinate); 8) poly(pentamethylene succinate).

The low superposability factor in some aromatic polyester molecules results in incomplete development of interchain interaction, in which π-electron interaction between benzene rings in neighbouring chains probably plays no minor role.

The superposability factor is closely linked with the structure of the initial aromatic component, with the relative arrangement of various structural groups in it, and with the degree of symmetry of the initial component[57]. The larger the value of this factor, the closer are the chains packed geometrically, the greater the possibility of more complete development of intermolecular interaction, and as a result the higher the softening temperature of the polymer.

The structures of the polyesters formed by ethylene glycol with terephthalic, isophthalic, and phthalic acids are shown diagrammatically in Fig. 11.[57] It is seen that the superposability factor should be highest with the terephthalic polyester (as a result of the greater symmetry of its molecule) and lowest with the phthalic polyester.

The aromatic rings in polyesters of isophthalic and especially phthalic acid act as a kind of wedge, separating the polymer chains and preventing them from being more closely packed. In such cases the additional rigidity of the polymer chain due to the aromatic rings is sometimes insufficient to compensate for the incomplete development of interchain interaction resulting from this separation.

Measurement of the activation energy of viscous flow for some polyesters containing aromatic units in their chain has shown that those of bicyclic dicarboxylic acids possess more rigid polymer chains than polyesters of monocyclic aromatic dicarboxylic acids, and the latter more rigid than polyesters of aliphatic dicarboxylic acids.

On passing from polyesters of *m*-dicarboxylic to those of *o*-dicarboxylic acids, as well as from polyesters of *p*-xylylene glycol to those of *m*-xylylene glycol, the density of packing of the polymer chains, *i.e.* the superposability factor, diminishes, an effect produced also by introducing a methyl side-chain into the glycol molecule.

The value of the superposability factor has a great effect also on the ability of polyesters to crystallise.

Aromatic polyesters comprising rigid macromolecules possessing high superposability factors are usually crystalline substances, while the ability to crystallise is greatly diminished in aromatic polyesters having low values of the factor. The greatest variation is found in the properties of polyesters obtained from "purely" aromatic components (polyarylates). The presence of aromatic rings joined together only by ester links in these polymer chains produces a very marked rise in the softening point [10,58].

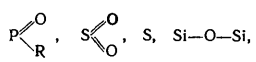
A similar effect of packing density and crystallinity on thermal stability can be traced in the polycarbonate series, where the general rule is that the tendency of the polymers to crystallise is weaker the more unsymmetrical and branched is the substituting group attached to the central carbon atom of the dihydric phenol [59].

Introduction of amide NHCO groups into the polymer chain has the opposite effect to that of ester groups, owing to formation in the first case of hydrogen bonds between the amide groups of separate macromolecules to produce a network. Their presence explains the higher melting points and mechanical strength which distinguish polyamides from polyesters and other polymers containing no hydrogen bonds.

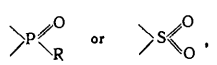
Substitution of alkyl groups on the nitrogen atom removes the possibility of hydrogen bonding, with the result that insoluble, hard, rigid, crystalline polyamides are transformed into soluble, soft, flexible products having considerably lower melting points and durability [60].

Complete manifestation of the second factor — interchain interaction — also requires maximum density of packing. The latter is associated with the structure of the initial aromatic component, with the presence and arrangement of substituents, and with the degree of symmetry of the macromolecule. An increase in density of packing of the chains improves the possibility of more complete development of intermolecular interaction, and hence is accompanied by a rise in the softening and melting points of the polymer. Thus it has been established, for example, that the introduction of rings (aromatic, hydroaromatic) into a polyamide macromolecule is in several cases accompanied by a rise in its melting point [11].

Introduction of groups containing hetero-atoms



into the macromolecule has a considerable effect on the properties of polyamides, the chief factor being the polarity of the group [56]. Thus replacement of a CH_2 group in a dicarboxylic acid by



results in a considerable rise in melting point and a decrease in solubility. Introduction of $-SiR_2.O.SiR_2-$ or $-S-$ makes the macromolecule more flexible, and, as a result of the presence of side-chains, diminishes the density of packing.

The breakdown in regularity in the macromolecules of mixed polyamides results in a weakening of intermolecular interaction owing to the diminished density of packing and the increased distances between the chains, as well as between corresponding amide groups involved in the formation of hydrogen bonds.

There is an important difference between the effects, on the properties of polymers of interchain forces of interaction (both dipole forces and hydrogen bonds) and valency cross-links: the former are strongly dependent on temperature, and rapidly become weaker as it rises, whereas the strength of cross-linking is independent of temperature over a wide range.

All the above facts provide evidence of the quite complicated character of the relation between the structure and the properties of polymers. This is not surprising when it is realised that the link between the macromolecular structure and the properties of the polymer in bulk is not direct but, as has recently been established, involves intermediate, so-called supermolecular structures. Research on the supermolecular structures of polymers has been widely developed during recent years, a leading position in this field being occupied by Soviet workers, mainly Kargin and his school.

Kargin *et al.* [61] suggested that polymers have a "bundle" structure, the formation of crystalline polymers being a very complicated process and involving a series of intermediate stages. Two types of aggregation of the macromolecules — into globules and bundles — are then possible. These are the primary structures, from which more complicated secondary structures are built up. In the former case further ordering involves the formation of macrocrystals from separate globules. In the latter case, completely crystallised bundles, tending to diminish their surface in virtue of thermodynamic considerations, join together to form strips. For the same reasons these latter join to form planar structures, sheets, from which crystals may ultimately be formed [62].

Little work has yet been done on the question of how the structure of the bundles and other intermediate formations affects the bulk properties of the polymer, or on how and to what extent the structure of the bundles is linked with that of the macromolecule itself and its monomer units. The general conclusion can obviously be drawn that a simple and fairly clear relation between the monomer structure and the bulk properties of the polymer is observed only when the intermediate steps in the packing of the macromolecules are governed by equally simple relationships. If however, the structure of the monomer units is such that this is impossible, the influence of these intermediate stages will so obscure the picture that it is now very difficult to establish simple relations between the monomer structure and the bulk properties of the polymer. In these cases we must confine ourselves to establishing most of the qualitative regularities, which make it possible to predict only the fundamental character of the variation in properties.

IV. DEPENDENCE OF THERMAL STABILITY ON REACTIVITY OF MACROMOLECULE

A very important factor in characterising the thermal stability of a polymer is its resistance to the action of atmospheric oxygen, water vapour, and other chemical reagents, as well as its tendency to degradation and cross-linking. All these changes take place rapidly at high temperatures, and therefore the liability of a polymer to undergo them is very important in assessing its possible practical uses.

Resistance to oxidation is a most important characteristic of a polymer. Reactions caused by the action of atmos-

pheric oxygen on polymers result in their degradation or cross-linking (or both simultaneously), which impairs their mechanical properties.

As Korshak *et al.*[63,64] have shown, polyamides on storage in air even at room temperature gradually oxidise and form peroxides; heating accelerates this process considerably, and results in oxidative degradation of the polyamides [12,65,66].

According to Harding and MacNulty[67] the main cause of the appearance of brittleness and loss in strength in a polyamide on being heated in air is oxidative degradation accompanied by hydrolysis.

Sharkey and Mochel[68] consider that in the oxidation of polyamides oxygen attacks the α-carbon atom of the amine residue according to the scheme

$$RCONHCH_2R' \xrightarrow{h\nu} R\dot{C}O + R'CH_2\dot{N}H,$$

$$R\dot{C}O + RCONHCH_2R' \rightarrow RCHO + RCONH\dot{C}HR',$$

$$R'CH_2\dot{N}H + RCONHCH_2R' \rightarrow R'CH_2NH_2 + RCONH\dot{C}HR,$$

$$RCONHCH(OH)R' \rightarrow RCONH_2 + R'CHO,$$

$$R'CHO + O_2 \rightarrow R'COOH.$$

Almost all polymers undergo oxidation by air, especially at high temperatures. Oxidation processes are accompanied by degradation of the polymer chains. Thus the degradation of polyesters on oxidation involves intermediate formation of free radicals, probably according to the general scheme for degradative reactions of this type[69]. The first stage is formation of a hydroperoxide, which then breaks down to form free radicals:

$$\ldots -O(CH_2)_4OCOR'CO- \ldots \xrightarrow{O_2} \ldots -O-\underset{\displaystyle OOH}{\underset{|}{CH}}(CH_2)_3OCOR'CO- \ldots \rightarrow$$

$$\rightarrow \ldots -O-\underset{\displaystyle O\cdot}{\underset{|}{CH}}(CH_2)_3OCOR'CO- \ldots + \ldots -OCH_2(CH_2)_3OCOR'CO- \ldots \rightarrow$$

$$\rightarrow \ldots -OCH(OH)(CH_2)_3OCOR'CO- \ldots + \ldots -O\dot{C}H(CH_2)_3OCOR'CO- \ldots$$

As a result of interchain interaction, free radicals can form a spatial network of a cross-linked three-dimensional polyester, and may also lead to further breakdown in the polyester chain:

$$-O\dot{C}H(-CH_2-)_3OCOR'CO- \ldots \rightarrow -OCH=CH_2 + CH_2-CH_2-OCOCO- \ldots$$

$$\ldots -O\dot{C}HROCOR'CO- \ldots \ldots -O-\underset{|}{CH}-ROCOR'CO- \ldots$$

$$\ldots -O\dot{C}HROCOR'CO- \ldots \rightarrow \ldots -O-\underset{|}{CH}-ROCO-R'CO- \ldots$$

These reactions occur especially readily in the case of polymers containing double bonds and tertiary hydrogen atoms in the macromolecule. Thus polypropylene is more readily oxidised than is polyethylene.

Polymers containing benzene rings or heterocycles of aromatic character (benzimidazole, pyridine, thiazole, oxadiazole, etc.) are distinguished by their great resistance to oxidation. The hydrogen atoms in these systems are very firmly bound, and therefore the peroxy-radical is unable to abstract them, which results in chain termination in the oxidising process. Therefore such polymers begin to oxidise only at high temperatures (400–600°).

Polyorganosiloxanes are very resistant to thermal oxidation, which is explained by the inertness of the organic radicals attached to the silicon atom resulting from the polarity of the Si–C bonds. The siloxane Si–O bond in polyorganosiloxane molecules has a well-defined polar character, and it therefore increases the polarity of the Si–C bond and correspondingly lowers the force effect of the oxygen molecule acting on the organic radicals which are attached to the polymer chain[39]. However, linear polyorganosiloxanes, like linear organic polymers, undergo thermal degradation more readily than do three-dimensional cross-linked polymers, since in linear molecules not only Si–C but also Si–O bonds are broken by the action of high temperatures.

The resistance of polymers to hydrolysis is greatly diminished at high temperatures. Hetero-chain polymers are especially sensitive to hydrolysis. Thus in polyamides

$$-NH-\overset{\displaystyle O}{\overset{\|}{C}}-$$

the polar character of the amide link –NH–C(=O)– makes it more sensitive to the action of various polar reagents. It is ruptured under the influence of acids, alkalis, water, amines, etc. Reactions including hydrolysis, acidolysis, aminolysis, etc. in most cases involve degradation of the polyamide macromolecule.

Rate of hydrolysis depends on the nature of the hydrolysing agent, the conditions of hydrolysis, and the structure of the polyamide. In the cold, polyamides are fairly stable to the action of hydrolysing agents; water does not act at all on them without heating. They dissolve at room temperature in concentrated acids — sulphuric, hydrochloric, formic, nitric, etc. — without appreciable degradation[70,71]. The rate of hydrolysis is greatly increased at high temperatures[72,73].

The various types of polyamides can be arranged in the following sequence of increasing resistance to hydrolysis

$$[-NRCO-]_x < [-NHCH_2NHCO(CH_2)_4CO-]_x < [-NH(CH_2)_6NHCOO(CH_2)_4OCO-]_x <$$

$$< [-NH(CH_2)_5CO-]_x < [-NH(CH_2)_6NHCO(CH_2)_4CO-]_x <$$

$$< [-NH(CH_2)_6NHCO(CH_2)_8CO-]_x <$$

$$< [-NHCHRCO-]_x < \left[\begin{array}{c} N-N \\ \| \quad \| \\ C \quad C-(CH_2)_6- \\ \diagdown \diagup \\ N \\ \| \\ NH_2 \end{array}\right]_x.$$

The most stable to hydrolysis are the polyaminotriazoles, and also the polybenzimidazoles, which withstand prolonged heating with acids and alkalis[28,74].

Molecular chains built up from silicon, oxygen, and various elements — aluminium, titanium, boron, tin, etc. — whose bonds are appreciably ionic in character, exhibit considerable sensitivity to water. Andrianov and his collaborators have shown[39] that the hydrolytic stability of silicon–oxygen–element bonds is greatly affected by the bonding between various elements in the polymer chain and by their organic framework.

Investigation of the hydrolytic stability of compounds of general formula $[(C_2H_5)_3SiO]_nM$ (where M represents an atom of aluminium, titanium, or tin) has established the sequence Sn > Al > Ti in the rate of hydrolysis.

The hydrolytic stability of polyaluminoorganosiloxanes was found to exceed that of various organosilicon compounds, which are cleaved by acid reagents. The great resistance to hydrolysis of $\gtrless$Si–O–Al$\lessgtr$ bonds compared with the $\gtrless$Si–O–Si$\lessgtr$ bond is explained by Andrianov[39] on the assumption that the action of an acid on polyalumino-siloxanes involves two reactions — rupture of the $\gtrless$Si–O–Al$\lessgtr$

bond and intermolecular condensation of the resulting hydroxy-groups on the silicon atom, with the formation of complicated polymeric molecules from chain fragments, which create steric hindrance to the development of acid hydrolysis of the $\rangle$Si–O–Al$\langle$ bonds.

Carbon-chain polymers are stable to hydrolysis.

Heating a polymer to high temperatures can cause the occurrence of two processes, degradation and cross-linking. Degradation is due to the rupture of chain molecules, with a progressive decrease in molecular weight of the polymer, and hence a deterioration in mechanical properties. Cross-linking involves the formation of bonds between the polymer chains, and is accompanied by an increase in molecular weight, which to some extent may tend to improve the physical and mechanical characteristics of the polymer as well as its thermal stability. The formation of a large number of bonds between separate macromolecules with the building up of a rigid network converts the polymer into a hard, brittle, infusible, and insoluble product. Most often both these processes take place in polymers at the same time, especially as the primary stages in both processes involve formation of free radicals, in the first case by the scission of carbon–carbon bonds, and in the second case by abstraction of hydrogen from CH_2 group.

For some time degradation and cross-linking in a polymer can in effect balance one another, so that it appears that no change has occurred in the polymer. As the processes continue, however, one of the two reactions begins to predominate, resulting in either rapid softening or a sudden breakdown in the material[75].

The resistance of a polymeric molecule to the action of high temperatures is governed by the strength not only of the bonds in the polymer chain itself but also of those linking atoms surrounding the main chain or forming side-chains, for example C–H bonds in hydrocarbons, C–F in fluorinated polymers, C–Cl in poly(vinyl chloride), etc., since their rupture is accompanied by degradative processes and results in a change in the structure and properties of the polymer.

This resistance is assessed quantitatively from the loss in weight of the polymer when it is heated at a specified temperature for a definite time.

Table 14 illustrates the thermal stability of polymers by the temperature at which they lose half their weight on being heated in a vacuum for 30 min[76,77]. On the basis of this work Madorsky[76,77] suggested the following sequence for the thermal stability of individual bonds and groups.

C–F > C–H > C–C > C–Cl

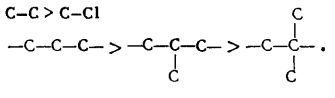
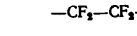
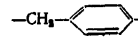
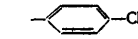
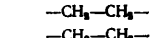
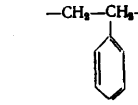
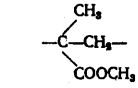
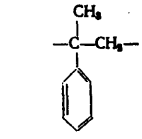


Table 15 gives the losses in weight of various polymers when heated at different temperatures for 24 h.

The thermogravimetric method has become widely used for determining the thermal stability of polymers. Figs. 12 and 13 give thermograms of polybenzimidazoles, from which it is clearly seen that appreciable loss in weight occurs only at 400–500° and above[28].

Sometimes a method based on measurement of the quantity of gaseous decomposition products evolved is used

TABLE 14. Thermal stability of polymers*.

Polymer	Structure	Softening temp., °C	T_η	$K_{350°}$, % min^{-1}	E, kcal mole^{-1}	Yield of monomer, %
Polytetrafluoroethylene		327	509	$2\cdot10^{-6}$	81	>95
Poly-p-xylylene		380—400	432	$2\cdot10^{-3}$	73	0
Polybenzyl		260—280	430	$6\cdot10^{-3}$	50	0
Polyethylene		135	404	$8\cdot10^{-3}$	63	<0.025
Polystyrene		145—160	364	$2.4\cdot10^{-1}$	55	40
Poly(methyl methacrylate)		155—180	327	5.2	52	>95
Poly-α-methylstyrene		160	286	226	55	>95

* T_η = decomposition temperature (loss of 50% of weight in 30 min);
$K_{350°}$ = rate of evolution of vapour;
E = activation energy of decomposition.

TABLE 15. Loss in weight of various polymers at different temperatures (in a vacuum).

Polymer	Loss in weight (%) after 24 h at			
	250°	350°	400°	450°
Polyphenylsiloxane	3.8	10.0	27.0	43.5
Polydimethylpolyphenylsiloxane	7.2	22.8	36.0	44.7
Polydiethylpolyphenylsiloxane	8.3	30.2	38.0	—
Polytetrafluoroethylene	1.3	2.1	2.5	—
Polychlorotrifluoroethylene	4.6	98.9	—	—
Poly(ethylene terephthalate)	5.3	68.0	—	—
Epoxide resin	22.7	93.1	—	—
Capron [poly-ε-caprolactam]	55.5	94.3	—	—

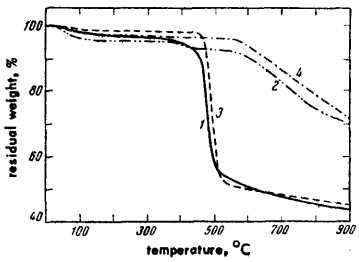


Fig. 12. Thermograms of polybenzimidazoles obtained from:
1) 1,2,4,5-tetraminobenzene and adipic acid;
2) 1,2,4,5-tetraminobenzene and isophthalic acid; 3) diaminobenzidine and adipic acid;
4) diaminobenzidine and isophthalic acid.

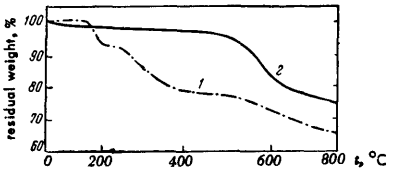


Fig. 13. Thermograms for polybenzimidazoles obtained from diaminobenzidine and:
1) ferrocene-1,1′-dicarboxylic acid; 2) imidazole-4,5-dicarboxylic acid.

to compare the thermal stabilities of polymers. Fig. 14 shows the relative rates of breakdown of three polymers, and it is evident that the polyarylate D-2 is extremely thermostable even at 400°.[35] Fig. 15 shows the extent of decomposition of the polyarylates D-1 and D-2 when heated at various temperatures for 1 h.[35] It is seen that appreciable breakdown of the polyarylates begins only above 400°.

According to Lee[78], the thermal degradation of polycarbonates is determined by the stability of the bonds linking atoms forming part of the macromolecule. Table 16 gives energy values for the various bonds in a polycarbonate, on the basis of which Lee suggests two possible

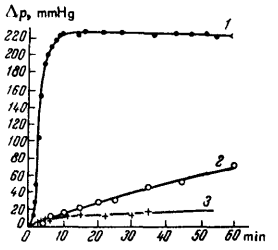


Fig. 14. Rate of thermal degradation at 400° of some polymers based on 2,2-diphenylpropane-*pp*′-diol determined from the pressure of the gases evolved:
1) epoxide resin (ED-6) hardened with 30% of maleic anhydride; 2) poly-(2,2-diphenylpropane-*pp*′-diol carbonate); 3) polyarylate D-2.

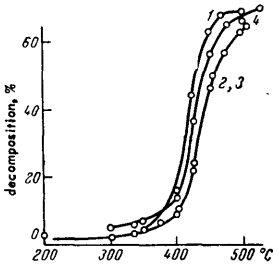
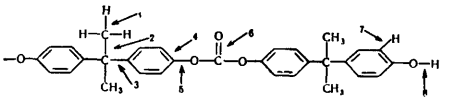


Fig. 15. Dependence of extent of decomposition of polyarylates D-1 and D-2 on temperature (maintained for 1 h):
1) D-1 obtained by equilibrium polycondensation; and D-2 obtained by: 2) equilibrium polycondensation; 3) interfacial polycondensation; 4) interfacial polycondensation.

TABLE 16. Energy of bonds in polycarbonate.

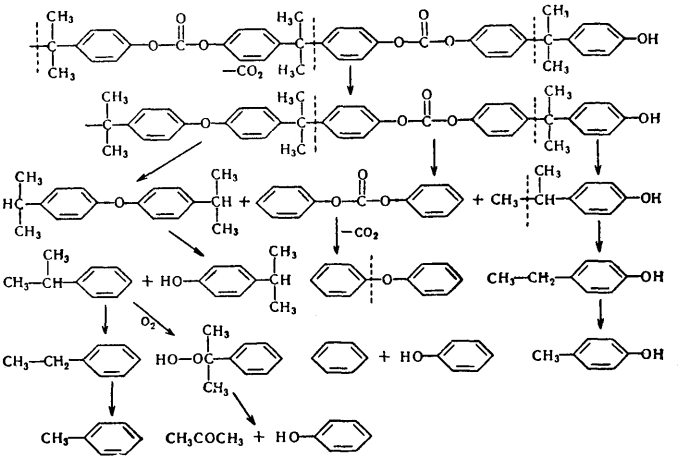


Serial No.	Bond	Bond energy, kcal mole^{-1}
1	C—H	98.7
2	C—CH_3	60.0
3	C—C	82.6
4	C=C	147.5
5	C—O	85.5
6	C=O	176.0—179.0
7	C≡C—H	102
8	O—H	101.5

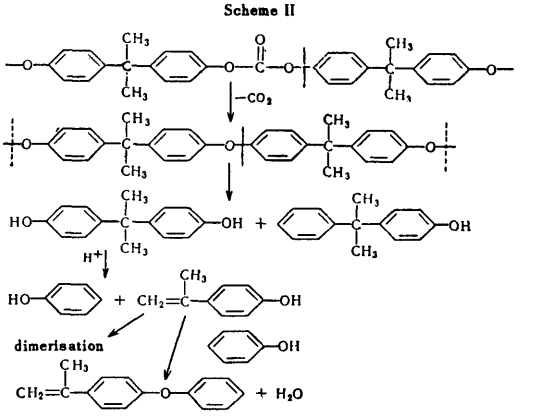
mechanisms of degradation. The accompanying Schemes I and II show that processes of thermal degradation are always accompanied by side-reactions, also resulting in cleavage of polymer chains, *e.g.* decarboxylation, hydrolysis, dehydration, etc.

Mechanism of degradation

Scheme I

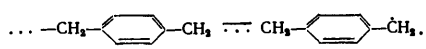


Scheme II

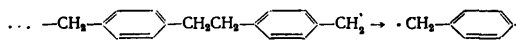


Regarding the degradation of polymers as a process involving the formation of free radicals, Grassie[79] explained the greater thermal stability of polymers containing aromatic rings in the chain, in comparison with vinyl polymers, by the ability of the unpaired electron in the former case to be delocalised along the whole polymer chain.

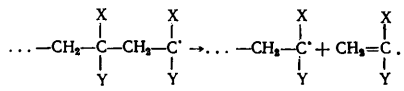
Therefore conditions are not created which would favour intramolecular disproportionation resulting in the splitting off of a terminal monomer unit (monomer), which can be represented in general by



In the degradation of poly-*p*-xylylene, for example, such units could be eliminated in the form of a diradical:



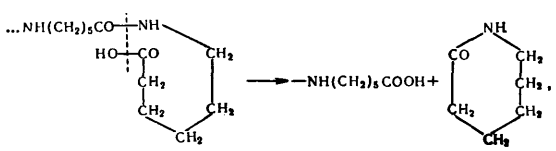
but, owing to its reactivity, the latter does not exist as such (in solution only at -78°), and will recombine again. Vinyl monomers other than polyethylene are degraded by high temperatures with the formation of monomers as final products:



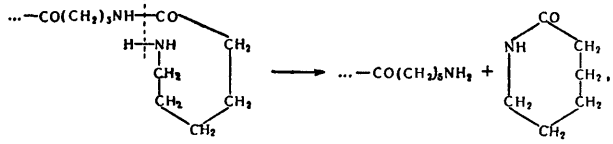
The role of the quaternary carbon atom involves the stabilising effect of the substituents X and Y on the resulting free radical, a decrease in reactivity of the macroradical, and hence the securing of intramolecular disproportionation with separation of the monomer. If one of the substituents X and Y is a phenyl group, its great resonance stabilisation effect makes the macroradical stable even in the presence of a quaternary carbon atom, and makes possible intramolecular disproportionation of the macroradical with separation of the monomer (*e.g.* the degradation of polystyrene).

We must also note the tendency shown by many polymers to form cyclic structures on degradation, especially if five–seven-membered rings can be obtained. Thus linear polyesters break down at high temperatures with the formation of cyclic esters[80]. According to Hill and Carothers[81], the ease with which this occurs depends on the structure of the monomer unit in the polyester and on the nature of the catalyst employed. Oxalic and carbonic esters undergo cleavage the most readily; when the monomer unit of the polyester contains 7–12 carbon atoms, the main decomposition products are dimeric esters; and with 13 or 14 carbon atoms a mixture of monomer and dimer is obtained. The presence of a larger number of atoms results in a monomeric ester. Various metal salts have been used as catalysts for the decomposition of polyesters[82].

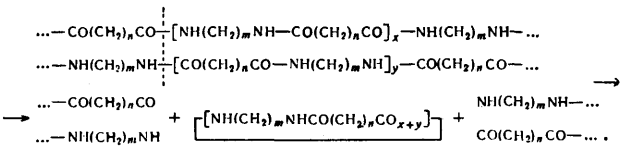
Cyclic as well as linear products have been detected in polyamides[9]. Ring formation is explained by the occurrence of exchange reactions between the macromolecules in the process of equilibrium polycondensation. These reactions also occur in the thermal degradation of polyamides. Rings can be obtained as a result of one of the reactions — (1) acidolysis



(2) aminolysis

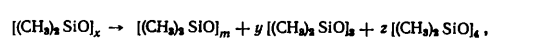


and (3) amidolysis



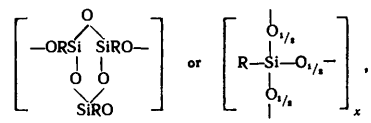
Small rings can be formed by reactions (1) and (2), whereas reaction (3) can give rings of any size.

Cyclic organosiloxanes have been observed as thermal degradation products of polyorganosiloxanes. Data have been published indicating that in polydimethylsiloxanes the molecular chains have a helical structure with 3–6 silicon atoms in a turn of the helix[39]. Under the influence of high temperatures such a structure provides conditions favouring the closure of six- and eight-membered rings with cleavage of the chains. Thus polydimethylsiloxanes, on being heated in a vacuum at around 300°, break down into cyclic oligomers of low molecular weight according to the scheme



where $m + 3y + 3z = x$.

In polyorganosiloxanes having a three-dimensional molecular structure



removal of a monomer unit or of a large segment from the polymer chain necessarily involves scission at three points, *i.e.* the rupture of two or three energetically stable Si–O bonds. In polyorganosiloxanes with bonds in three dimensions, therefore, no degradation of the molecular chains at Si–O bonds is observed even at 550°, independently of the nature of the organic radical[39].

The resistance of polymers to heat, light, and oxidising processes can be increased by the addition of stabilisers to the polymer. Since the primary act in the action of heat, oxygen, light, radiation, etc. on polymers is the formation of free radicals, the main role of stabilisers is to prevent such formation or inhibit the radical reactions.

Stabilisers have been selected for each class of polymers, their number being very large. Thus antioxidants are used to protect polyethylene from thermal oxidation, the best of them being mixtures of phenols and amines[83]. Antioxidants can also delay photochemical oxidation (aging under the influence of light) for some time. An effective remedy against photochemical oxidation and the action of radiation on polyethylene and rubber is gas black (2%),

whose stabilising effect is due to its ability to absorb free radicals.

Stabilisers for poly(vinyl chloride) slow down the elimination of hydrogen chloride, also preventing the formation of double bonds and being at the same time antioxidants and ultraviolet-absorbers. They include salts of carboxylic acids, thioplasts, the ammonium salt of the copolymer of styrene and maleic anhydride, carboxylic esters, organotin compounds, etc.[84]

Various substances have been suggested for the protection of polyamides from the action of oxygen, heat, and light, including copper compounds, alkaline phosphates and phosphites with alkali-metal halides, aluminium and manganese salts, finely divided powders of readily oxidisable metals — Mg, Al, Cr, Ca, Sr — and also several organic compounds, in particular those such as biphenyl and phenyl-1-naphthylamine, which have proved extremely effective for protecting polyamides from oxidative degradation [12].

The problem of producing stabilisers for highly thermostable polymers has not yet been solved. A possible method for its solution is the suggestion by Berlin *et al.*[85] that polymers having a system of conjugated multiple bonds should be employed as stabilisers.

The importance of the stabilisation of polymers in processing and service has attracted the close attention of research workers to this question, as has been reflected in numerous papers and monographs[84,86].

V. NEW THERMOSTABLE POLYMERS

Polymers employed at the present time can operate at temperatures up to 200°. Fig. 16 illustrates the working range for various polymers on the basis of Nowak's result[6]. It is seen that silicone and fluorine-containing polymers are the most thermostable, and can operate for a long time at temperatures reaching 200°. The use of polymers of other classes is confined to lower temperatures.

The novel thermostable polymers obtained by one of us together with Vinogradova[58], the polyarylates (see Table 17), have a higher range of working temperatures, as has been shown by the investigations of their properties by Slonimskii and Askadskii[87].

Fig. 17 compares polyarylates, based on terephthalic and isophthalic acids and phenolphthalein, with poly(methyl methacrylate) and a polycarbonate (makrolon)[87]. These polymers can function as structural materials up to the following temperature limits: (1) poly(methyl methacrylate) 70°, (2) polycarbonate 140°, (3) polyarylate F-1 200°, and (4) polyarylate F-2 260°. Several polyarylates are capable of operating at still higher temperatures. It is thus obvious that polyarylates considerably extend the range of thermostable polymers.

Fig. 18 shows the dependence of tensile strength on temperature for several rubbers[1]. Silicone rubber is seen to be the most thermostable, since it retains adequate strength even at 300°, when the other rubbers have already lost their strength.

Thermal stability can be characterised also by the temperature dependence of hardness. Fig. 19[1] illustrates data for nylon, Teflon, and reinforced Teflon. The relationship is seen to be in general similar to that in Fig. 18.

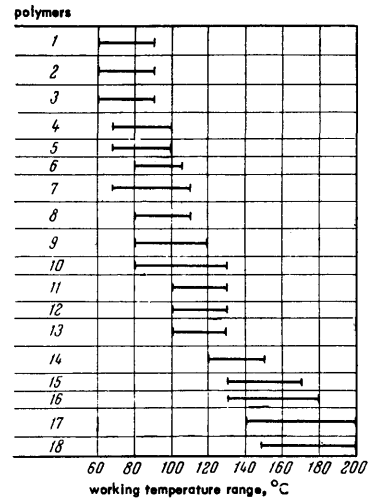


Fig. 16. Operating range for various polymers, bounded by limiting temperatures:
1) unmodified and modified poly(vinyl chloride); 2) ordinary and modified polystyrene; 3) rubbers based on purely organic latices; 4) polyacrylates and polymethacrylates; 5) polyolefins; 6) polyamides; 7) linear polyurethanes, unplasticised and plasticised; 8) unsaturated polyester resins; 9) modified polyester resins; 10) epoxide resins; 11) cross-linked polyurethanes; 12) polycarbonates; 13) linear terephthalates; 14) cross-linked terephthalate resins; 15) fluorinated elastomers; 16) siloxane elastomers; 17) ordinary and modified silicone resins; 18) rigid fluorinated polymers.

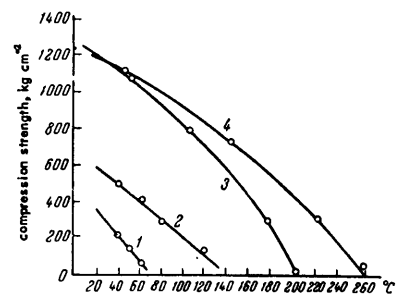
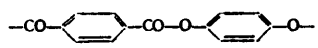
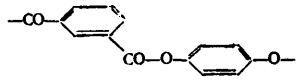
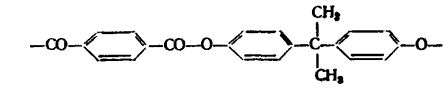
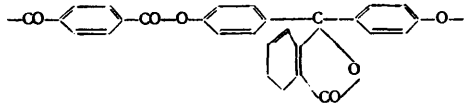
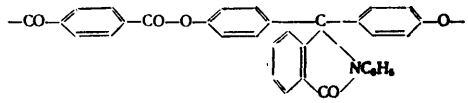
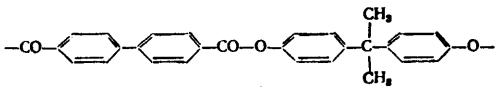
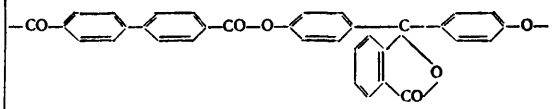
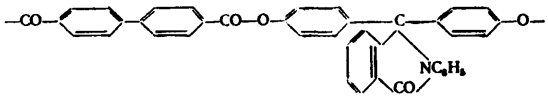
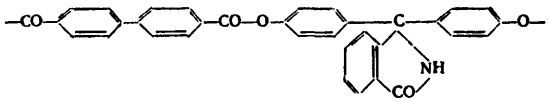
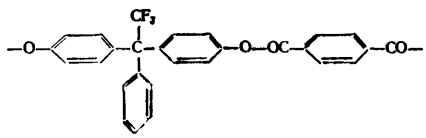
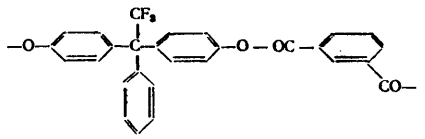
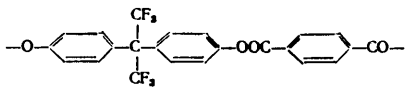
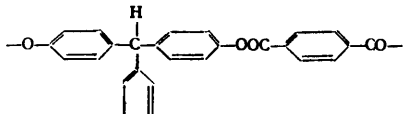
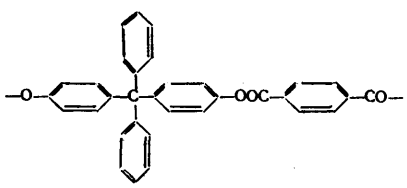


Fig. 17. Range of operating temperatures of polymers:
1) poly(methyl methacrylate); 2) poly-(2,2-diphenylpropane-*pp'*-diol carbonate); 3) polyarylate F-1; 4) polyarylate F-2.

We shall now examine individual classes of polymers and recently prepared thermostable compounds.

As already pointed out in Section II (Fig. 2), among the immense number of polymers only the following groups have members with a thermal stability above 300° — (1) stereoregular polyhydrocarbons, (2) unsaturated polyhydrocarbons, (3) perfluorohydrocarbons, (4) polyesters,

TABLE 17. The most important polyarylates[58].

Brand	Formula of monomer unit	Softening temp., °C
G-2		>500
I-1		>300
D-2		~350
F-2		~320
F-7		305
D-6		~410
F-4		~350
F-9		~350
F-12		~310
D-11		~310
D-12		~300
D-15		~350
D-17		~290
D-19		~300

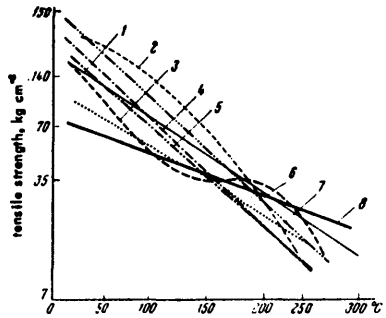


Fig. 18. Temperature dependence of tensile strength for various rubbers:
1) butyl rubber; 2) natural rubber; 3) Hypalon; 4) styrene–butadiene rubber; 5) nitrile rubber; 6) polyacrylate rubber; 7) neoprene; 8) silicone rubber.

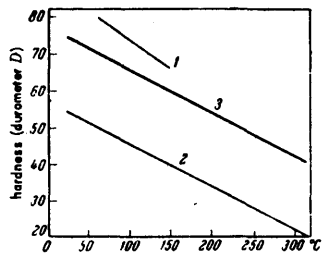


Fig. 19. Temperature variation of hardness for:
1) nylon; 2) polytetrafluoroethylene; 3) reinforced polytetrafluoroethylene.

(5) polyamides, (6) carbocyclic chain polymers, (7) heterocyclic chain polymers, (8) organoelementary polymers, and (9) inorganic polymers. Let us examine in this order recently published work on the synthesis and investigation of thermostable polymers.

Stereoregular Polymers

Stereoregular polymers include several compounds melting above 300°, which are listed in Table 9. The most thermostable are the polymers of *o*-methylstyrene (melting at 360°) and of 3,3-dimethylbut-1-ene (370°).

Nametkin *et al.*[42] have obtained isotactic polymers of allyldimethylphenylsilane (m.p. 300°) and of diallyldimethylsilane and diallylmethylphenylsilane, which are extremely high-melting substances (m.p. 400–410°).

Unsaturated Polyhydrocarbons

Among the numerous class of unsaturated polyhydrocarbons only those which have a continuous chain of conjugation in the macromolecule are of outstanding thermal stability[88,89]. The simplest representative of this type is "carbyne", obtained by Korshak *et al.*[90] It is formed by

the oxidative dehydropolycondensation of acetylene by the reaction

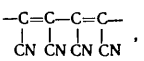
$$x\,HC{\equiv}CH \xrightarrow{\text{oxidation}} (-C{\equiv}C-)_x.$$

Carbyne is an insoluble, hard black powder. When heated in the absence of oxygen, it is converted into graphite at 2300°. It is semiconducting.

Polymethine $(CH=CH)_x$ was obtained by Kern[91] by the action of concentrated sulphuric acid on poly(vinyl alcohol). It withstands heating to 600°. It is a semiconductor above 150°, and is used for the manufacture of light-polarising materials. This same polymer has been obtained by Berlin[92] by the dehydrochlorination of poly(vinyl chloride) in the presence of sodium pentyloxide.

Polyvinylene hydrocarbons having the structure $[C(CH_3)=CH]_x$ have been obtained by Kargin *et al.*[93] from acetone by polycondensation in the presence of zinc chloride. Recently a large number of polyvinylene hydrocarbons have been prepared by the polymerisation of acetylene and its homologues[94]. They have the structure $[C(R)=CH]_x$, and are distinguished by high thermal stability and the presence of semiconductor properties.

Beneš *et al.*[95] prepared polymers of dicyanoacetylene by polymerisation in the presence of anionic catalysts. The polymer has the structure



and does not melt below a red heat.

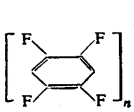
Perfluorohydrocarbons

Apart from the members which have now been known for some time — polytetrafluoroethylene, polychlorotrifluoroethylene, and copolymers of hexafluoropropene with tetrafluoroethylene and vinylidene chloride (Viton A) — several new members of this extremely interesting group of thermostable polymers have been described. Investigation has shown that polymers containing the maximum quantity of fluorine are the most interesting.

Several defects of vinyl polymers can be eliminated by replacing hydrogen by fluorine, since the energy of the C–F bond is greater than that of the C–C and C–H bonds. Completely fluorinated polymers are known to possess higher thermal and chemical stability than their hydrocarbon analogues[96].

Polymers of styrenes containing less than three fluorine atoms in the aromatic ring do not possess interesting properties; the homopolymer of pentafluorostyrene $(C_6F_5CH=CH_2)_x$ and copolymers of *m*-trifluoromethylstyrene and butadiene exhibit better mechanical properties and greater thermal stability than do polymers obtained from styrene itself[97]. Polymers have been prepared of β-fluorostyrene $(C_6H_5CH=CHF)_x$ with softening points of 240–260°, ββ-difluorostyrene (~ 180°), αβ-difluorostyrene (about 220°, with decomposition), and αββ-trifluorostyrene (185–190°).[97,101]

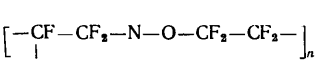
Fluorinated aromatic polymers of the type of perfluoropolyphenylenes



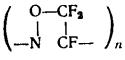
possess very high thermal stability. Perfluoropolyphenylene was obtained by the reaction of tetrafluoro-*p*-diiodobenzene with copper powder, and contained up to eleven phenylene residues. Perfluorophenylene oxide, obtained by heating sodium or other pentafluorophenoxide, was also of low molecular weight. No information is yet available on the thermal stability of these polymers[97,101].

Great interest attaches to tetrafluorophthalic acid, which can be used for the synthesis of polyesters and polyamides[98].

Recently a novel type of polymer has been prepared, containing perfluoroalkyl groups and the N–O bond in the macromolecule. These polymers are obtained by the copolymerisation of perfluoroalkylnitroso-compounds with fluorinated ethylenes. They have elastic properties and high chemical stability. Thus the copolymer of trifluoronitrosomethane and tetrafluoroethylene consists of repeating

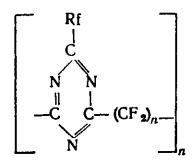


units. It is soluble only in chlorofluorohydrocarbons, retains its elasticity down to -30°, has a glass temperature of -51°, and decomposes on being heated to 210°; it can be vulcanised with benzoyl peroxide[99]. The homopolymer of trifluoronitrosoethylene



forms an elastomer which is stable up to 400°; it is very resistant to the action of nitric acid[100].

The perfluoropolytriazine elastomers described by Brown[102] are stable in air up to 350–410°, and retain their properties unchanged after being boiled with fuming nitric acid for 24 h. These polymers are obtained by the condensation of perfluorodiamidines with perfluoroamidines, which results in the formation of triazine rings



Rf = perfluoroalkyl.

Unfortunately, almost nothing is known of stereoregular perfluorohydrocarbon polymers, which should be of great interest. Only isotactic perfluoropropylene (m.p. 110–120°) is known[103].

Polyesters

From the number of known representatives, polyesters represent an immense group of polymers. All aliphatic polyesters have low melting points. Only polyesters of aromatic dicarboxylic acids and ethylene glycol have fairly high melting points[8] — poly(ethylene terephthalate) 265°, poly(ethylene biphenyl-*pp'*-dicarboxylate) 330°, poly(ethylene diphenylmethane-*pp'*-dicarboxylate) 320°, poly(ethylene azobenzene-*pp'*-dicarboxylate) 365°, and poly(ethylene dithioterephthalate) 335°. Polycarbonates — polyesters of dihydric phenols and carbonic acid — likewise are not characterised by high melting points[59]. Only the polycarbonate formed by diphenylmethane-*pp'*-diol

melts above 300°, and that from 1,2-diphenylethane-*pp'*-diol at 290–300°. The highest melting points are possessed by polyesters of aromatic dicarboxylic acids and dihydric phenols, which have the general name "polyarylates".[58] Table 17 lists the most thermostable representatives of this group.

The presence of good electrically insulating properties in polyarylates, and their ability to form films and fibres, make this class extremely promising for the manufacture of all kinds of thermostable goods.

In the absence of oxygen, polyarylates withstand prolonged heating at high temperatures (300–400°). Oxidising processes occur at an appreciable rate only above 250°. With all resins, appreciable gas evolution starts on heating in an atmosphere of nitrogen above 400°, and rapidly intensifies with rise in temperature, reaching 20% of the original quantity of polyarylate at 500° (see Figs. 14 and 15).

Polyamides

Several polyamides also have high melting points[9]. In most cases they contain residues of aromatic diamines or aromatic dicarboxylic acids in the macromolecule, as is evident from Table 18.

Aliphatic polyamides oxidise comparatively easily at high temperatures. Aromatic and hydroaromatic polyamides are considerably more resistant to oxidation.

Cyclo-Chain Polymers

This class of polymers, which has recently attracted great attention from research workers, contains benzene, naphthalene, cyclohexane, and other carbocyclic rings, as well as various heterocyclic rings, in the main chain. We shall term the first group "carbocyclochain", and the second group "heterocyclochain", polymers. Koton[120] has given a detailed account of progress in the field of carboheterocyclochain polymers. The same questions have been considered in other reviews[121,122].

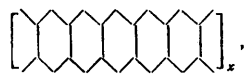
TABLE 18. Polyamides having high melting points.

Starting materials		Melting or softening point, °C	Ref.
diamine	dicarboxylic acid		
Hexamethylenediamine	terephthalic	350 (decomp.)	104
»	biphenyl-*pp'*-dicarboxylic	360 (decomp.)	105
»	2,5-dihydroxyterephthalic	334 (decomp.)	105
»	benzene-*p*-diacetic	320	106
»	di-*p*-carboxyphenyl ketone	350	107
»	*trans*-hexahydroisophthalic	310	108
»	*trans*-hexahydroterephthalic	360 (decomp.)	108
Piperazine	adipic	330	109
»	suberic	300	110
»	4-oxosebacic	350	110
»	terephthalic	400 (decomp.)	111
Cyclohexane-*trans*-1,3-diamine	adipic	300	112
Ditto	azelaic	300	112
Cyclohexane-1,4-diamine	adipic	400	105
Ditto	biphenyl-*mm'*-dicarboxylic	390	105
Bis-(4-amino-3-methylcyclohexyl)methane	terephthalic	300	113
Bis-*trans*-4-aminocyclohexylmethane	adipic	310	114
m-Phenylenediamine	*pp'*-dicarboxytriphenylphosphine oxide	340	107
p-Phenylenediamine	ditto	340	107
p-Xylylenediamine	succinic	360	115
Ditto	adipic	340	115
»	terephthalic	350	115
m-Xylylenediamine	terephthalic	300	116
Benzidine	adipic	400	117
»	sebacic	375	117
»	terephthalic	500 (decomp.)	118
Diphenylmethane-*pp'*-diamine	adipic	350	105
Ditto	terephthalic	420	117
mm'-Dimethyldiphenylmethane-*pp'*-diamine	adipic	324	119
Diphenylethane-*pp'*-diamine	adipic	400	105

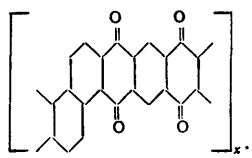
Carbocyclochain Polymers

There are many thermostable carbocyclochain polymers. Poly-*p*-phenylene

is an insoluble powder which does not melt below 530°, and withstands unchanged prolonged heating at 230–240°.[123] Extremely thermostable products were obtained by Pohl and Engelhardt[124] by condensing 1,2,4,5-tetrabromobenzene in the presence of a potassium–sodium alloy, these being cyclic "strip" polymers and having the structure



as well as by the condensation of pyromellitic acid with aromatic compounds (biphenyl, terphenyl, naphthalene, anthracene), yielding polymers of the type



The same type of polymer structure occurs in carbonised or graphitised fibres[125]. They are obtained from viscose rayon which has been heat-treated, first at 800–900° and then at 2700–2900°:

$$(C_6H_{10}O_5)_n \xrightarrow{800-900^\circ} (C_{36}H_5O)_n \xrightarrow{2700-2900^\circ} (C_{36}H)_n.$$

viscose rayon — carbonised (carbon fibre) — graphite fibre

These fibres and fabrics are distinguished by high thermal stability. They are employed fpr the manufacture of rocket nozzles, filters for hot gases, high-temperature thermal insulation, etc.

Insertion of methylene groups between aromatic rings makes macromolecules more flexible, often with preservation of the thermal stability. Thus polyarylenemethyls, obtained by Vansheidt *et al.*[126] by the polycondensation of formaldehyde with aromatic hydrocarbons, have high melting points — 350° with 1,2,4,5-tetramethylbenzene, 408° with 1,2,3,5-tetramethylbenzene, and 295° with anthracene.

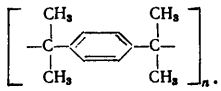
This group includes the phenol–formaldehyde resins, which are distinguished by appreciable thermal stability, especially in the series of modifications which have been described recently. Table 19 gives data on the thermal stabilities of phenol–formaldehyde resins as a function of the time of exposure. Furfuraldehyde–acetone and other resins based on furfuraldehyde are also characterised by high thermal stability[128].

We may also note poly-*p*-xylylene

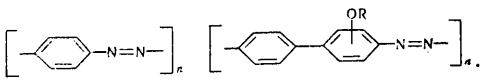
TABLE 19. Thermal stability of phenol–formaldehyde resin[127].

Temperature, °C	Duration
1000–1500	seconds
500–1000	minutes
250–500	hours
200–250	days
Below 200	indefinitely long

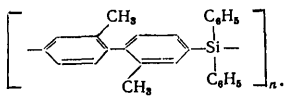
which was obtained by Szwarc [19] by the pyrolysis of *p*-xylene. In a vacuum it melts at 400°, but in air it decomposes at 225°.[129] Its homologue poly-*p*-diisopropylbenzene (polytetramethylquinodimethide) was obtained by Korshak and Sosin[130] by a reaction of polyrecombination (m.p. 300°).



Polyazobenzenes, obtained by polyrecombination, also contain a system of conjugated bonds and possess thermal stability up to 600°[131]



An extremely interesting silicon-containing polymer has been obtained by polyrecombination from diphenylsilane

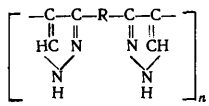


It is very thermostable, and does not char on prolonged heating up to 900°, when its loss in weight is only 5%.[132]

Heterocyclochain Polymers

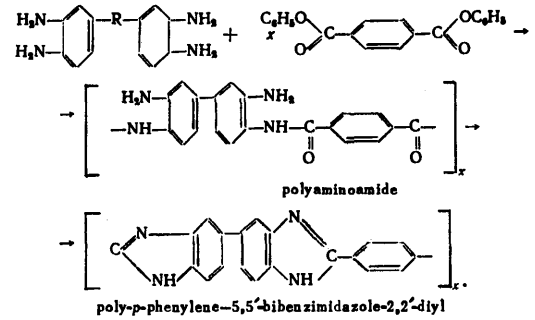
Heterocyclochain polymers form a very promising group of thermostable compounds, characterised also by great chemical stability. At the present time polymers have been described containing in the chain pyrazole, imidazole, triazole, quinoline, pyridine, oxadiazole, thiazole, pyromellitimide, and triazine rings.

Polymers containing pyrazole rings in the chain, especially when an unsubstituted NH group is present in the ring, have thermal stabilities reaching 400–500°. Polypyrazoles of this type were first obtained by the polycyclisation of bisdiazoalkanes with butadiynes, and have the structure



Their improved thermal stability compared with polypyrazoles in which the nitrogen atom is substituted is explained by the formation of hydrogen bonds[29,133].

Polybenzimidazoles form a group of exceptionally thermostable polymers. Especially high thermal stability is characteristic of those obtained from aromatic tetramines and aromatic dicarboxylic acids by the reaction



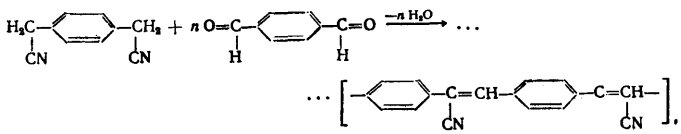
polyaminoamide

poly-*p*-phenylene–5,5′-bibenzimidazole-2,2′-diyl

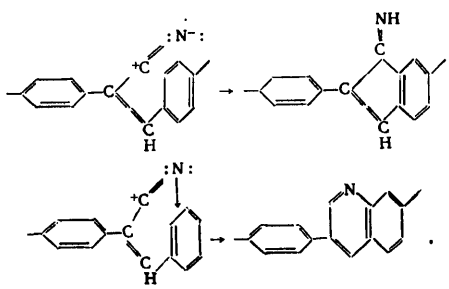
Several of these compounds have been obtained by Marvel and his coworkers[28,134], Korshak *et al.*[135], and other investigators[136]. The most interesting members of this group are listed in Table 20.

Polybenzimidazoles obtained from aliphatic acids begins to decompose at 450–500°, whereas their aromatic analogues break down appreciably only at 500–600°, and in an atmosphere of nitrogen a loss in weight exceeding 30% occurs only at 900°. Decomposition is more vigorous in air. Figs. 12 and 13 give thermograms illustrating the high thermal stability of aromatic and organoelementary polybenzimidazoles[28,134].

Reaction of $\alpha\alpha'$-dicyano-*p*-xylene with terephthalaldehyde



gives a polymer which after heat-treatment at 550° is thermostable[137]. The absence of the characteristic absorption of nitrile groups and double bonds from the infrared spectra indicates that the heat-treatment is accompanied by cyclisation with formation of a quinoline group in the chain or of an iminoindene structure



Polydicyanoterephthalidene does not lose more than 2% of its weight after heat-treatment at 550° followed by further heating at 550° for 30 min.[137]

TABLE 20. Properties of polybenzimidazoles[28,134,135].

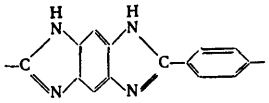
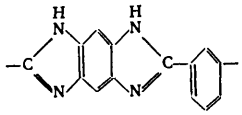
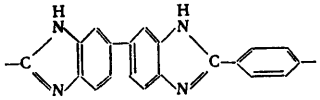
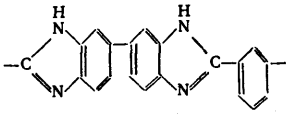
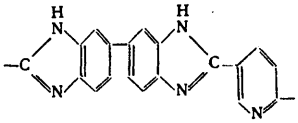
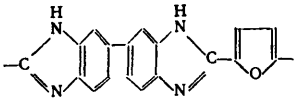
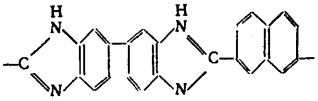
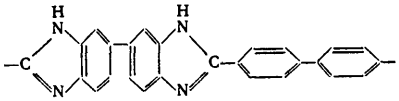
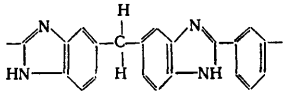
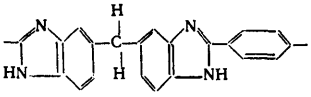
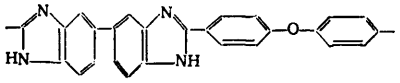
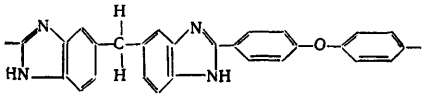
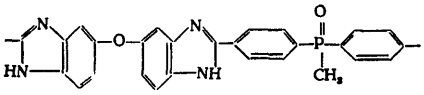
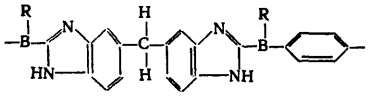
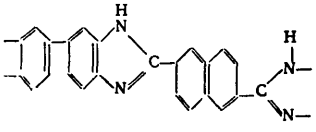
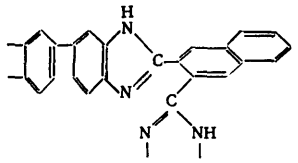
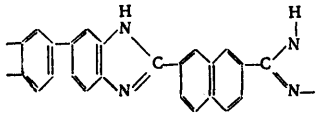
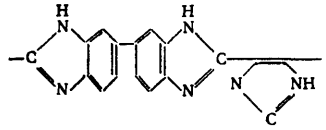
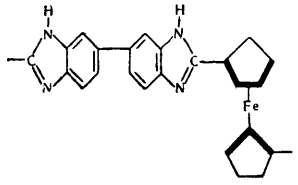
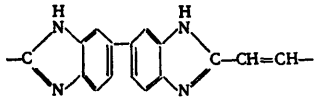
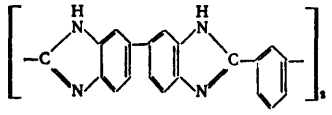
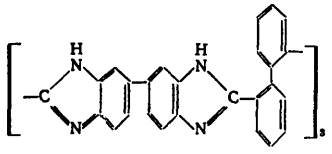
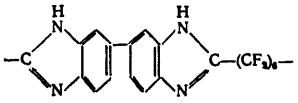
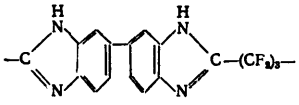
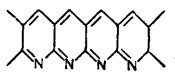
Monomer unit	Softening temp., °C	Loss in weight on heating in current of nitrogen, wt. %			
		400°	500°	550°	600°
	—	2.8	1.0	1.9	4.0
	—	0.7	0.3	1.4	1.4
	—	1.0	0	1.7	1.0
	—	0.6	0.4	1.3	2.2
	—	0.2	0.5	1.4	2.7
	480 (decomposition)	1.4	2.6	2.3	2.0
	—	0.4	0.8	1.2	3.7
	—	0.3	0.8	0.3	2.1
	380—390	—	5.16	15.45	31.30
	400—410	—	3.44	7.95	15.35
	460—470	—	5.44	7.48	10.20
	350—370	—	3.40	7.24	16.20
	380—400	—	27.50	39.80	47.85
	500	—	2.64	7.16	12.80
	—	—	5.0	10	15

TABLE 20 (contd.)

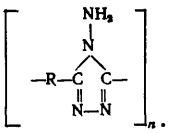
Monomer unit	Softening temp., °C	Loss in weight on heating in current of nitrogen, wt. %			
		400°	500°	550°	600°
	—	—	25	20	35 (700°)
	—	—	25	30	40 (700°)
	—	5	5	7—10	
	—	—	25	25	30
	—	—	20	—	25
	—	—	—	—	—
	—	—	20	—	25
	—	—	30	—	35
	—	—	40	—	50

By heat-treating polyacrylonitrile, Topchiev *et al.*[138] obtained a cyclic polymer to which they ascribed the structure



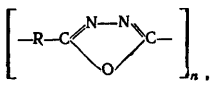
Polymers of this type are characterised by exceptional thermal stability, do not burn when introduced into a flame, and possess valuable semiconductor properties.

Polyaminotriazoles obtained by the polycondensation of hydrazine with aliphatic dicarboxylic acids have melting points of around 200–340°



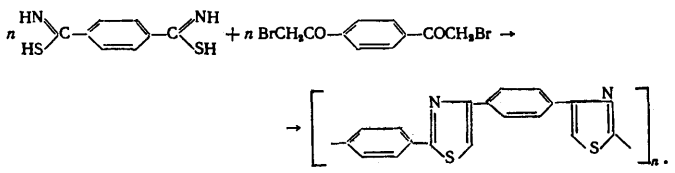
They are not decomposed on being boiled with concentrated acids and alkalis [139,140].

By the reaction of bistetrazoles with chlorides of dicarboxylic acids Abshore and Marvel [141] obtained polyoxadiazoles of general formula

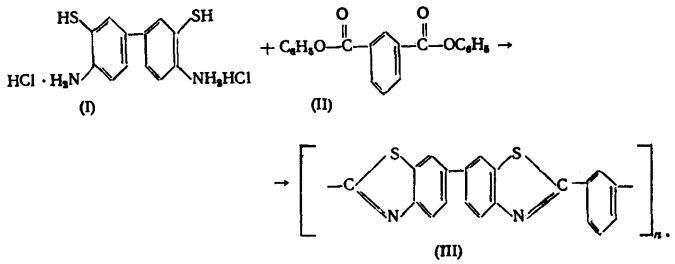


which were also stable up to 500°. When the polyoxadiazole obtained from *p*-phenylene–bistetrazole and terephthaloyl chloride was heated in air at 350° for 12 h, the loss in weight was 9.4%. Simpler methods have now been developed for preparing polyoxadiazoles, by the dehydration of polyhydrazides [142].

Polycondensation of *p*-bisbromoacetylbenzene with various dithioamides yields polymers containing repeating thiazole rings in their chain, characterised by stability up to 350°: [143]



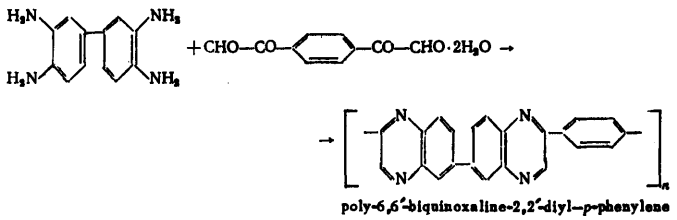
Polybenzothiazoles are formed also by the condensation of 3,3′-dimercaptobenzidine with aromatic dicarboxylic acids or their derivatives (dinitriles, diamides), in *NN*-diethylaniline or polyphosphoric acid solution, by the reaction



(I) (II) (III)

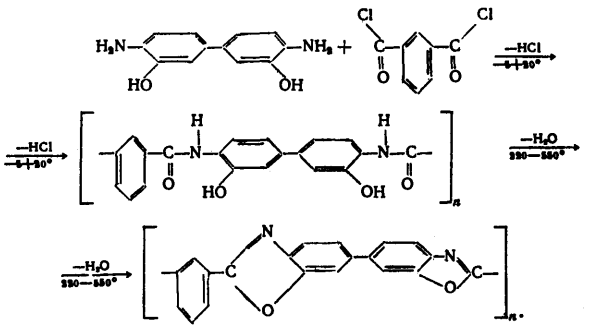
The resulting "precondensate" is precipitated with petroleum ether; on further heating at 400° for 1 h it is converted into polybenzothiazole. Poly-6,6′-bibenzothiazole-2,2′-diyl–*m*-phenylene (III) loses no weight at 538°, and at 593° its loss in weight is only 6%. [144]

Novel thermostable heterocyclochain polymers, the polyquinoxalines, have been described, which are stable in air at 500°, and in nitrogen lose 20% of their weight at 800°. They are obtained by the condensation of aromatic tetramines with tetracarbonyl compounds (the carbonyl groups should be located in the α position with respect to one another) [144–146]:

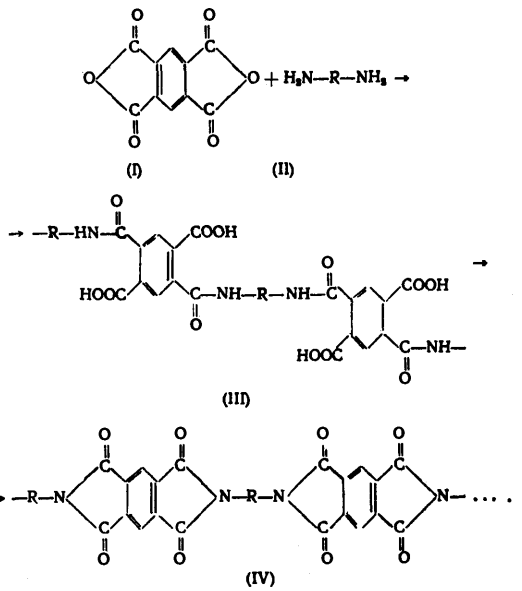


poly-6,6′-biquinoxaline-2,2′-diyl–*p*-phenylene

Polybenzoxazoles, synthesised by Takashi and his coworkers [147], have also proved to be extremely thermostable, withstanding 600° without change, and still retaining 80% of their weight at 900°. They are obtained in two stages:



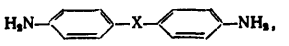
Pyromellitimide polymers are of particular interest [30,31]. They are obtained by the condensation of pyromellitic anhydride with diamines:



(I) (II) (III) (IV)

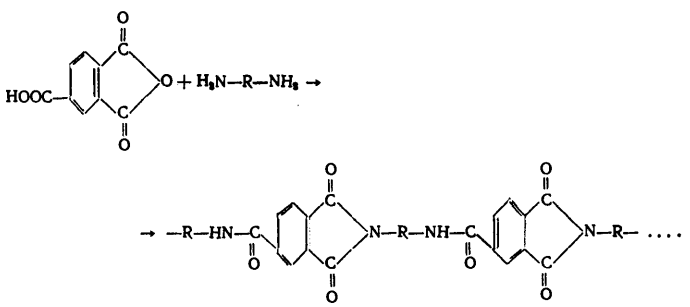
As a consequence of intramolecular ring-closure in the pyromellitimide system, the compound (III) becomes a bifunctional reagent, capable of forming linear polymers (IV). A disadvantage of these polymers is their infusibility and insolubility, which make the manufacture of articles difficult, while the liberation of water at the final stage limits their application. However, by using the soluble intermediate product (III), polypyromellitamide, formed in the first stage of the reaction, films can be obtained which can then be converted by cyclisation into the final polypyromellitimide[31].

Jones *et al.*[30] investigated the behaviour in this reaction of various diamines — *p*- and *m*-phenylenediamines, naphthalene-1,5(1,8 and 2,7)-diamines, 2,6-diaminopyridine, benzidine, and diamines of the type



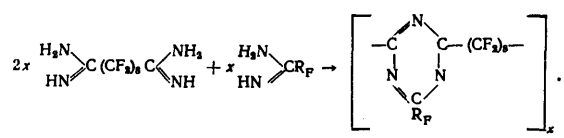
where X = O, SO_2, CH_2, CO. Polymers obtained from *m*-phenylenediamine, benzidine, and di-*p*-aminophenyl ether resist the action of solvents, possess high dielectric constants, and do not melt. The best mechanical properties and thermal characteristics are shown by films based on di-*p*-aminophenyl ether, the properties of the film being preserved after thermal treatment at 275° for 12 months.

Polycondensation of trimellitic anhydride with diamines yields imido-amide polymers:



They are somewhat inferior to pyromellitimide polymers in resistance to heat and oxidation[30].

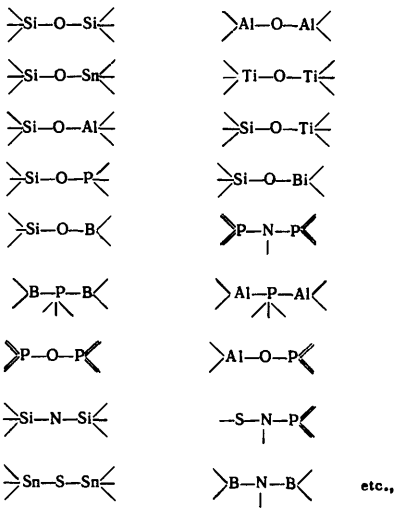
Brown[102] obtained a fluorinated polymer containing triazine rings in the chain by the pyrolysis of a perfluorodiamidine with a perfluoromonoamidine:



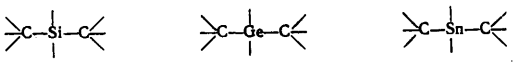
This polymer is thermostable up to 450°, and also possesses exceptional resistance to the action of fuming nitric acid (its properties remaining unchanged after 24 h). Losses in weight after heating in air at 470° and 475° for 30 min are 31% and 51% respectively.

Organoelementary Polymers

Polymers in this group are often extremely thermostable. Those containing the following types of bonds in their chain



are attracting great attention and are being intensively investigated. These elements can also be linked with carbon and with one another, for example

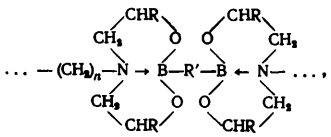


Polymers which do not contain carbon in the main chain of the macromolecule have been termed by Andrianov polymers with inorganic main chains. From a study of them he concluded[39] that the stability of the E–E bond is greater the less ionic in character are such bonds forming the main chain, *i.e.* the closer to the electronegativity of the carbon atom is the mean electronegativity of the two elements forming the bond.

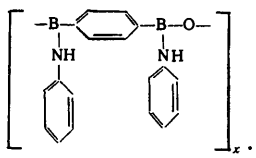
Among organoelementary polymers, the most detailed study has been made of polyorganosiloxanes and polymetalloorganosiloxanes, whose chains are built up from alternating atoms of electropositive silicon and another element (Al, Sn, Ti) and electronegative oxygen. Siloxanes, based on $-\overset{|}{\underset{|}{Si}}-O-$ bonds, exist in the form of oils, elastomers, and plastics. The stability of the material depends on the organic substituent attached to the silicon atom, diminishing in the sequence methyl > phenyl > ethyl. Polymers resistant to heat and hydrolysis are also formed when the oxygen bridge is replaced by phenylene residues. The Si–O–Si and Al–O–Al chains reproduce the skeleton of naturally occurring inorganic polymers — quartz and aluminosilicates — and are thermally and hydrolytically stable. The metalloorganosiloxanes synthesised by Andrianov[39] have high thermal stability (up to 600°) and good solubility. Since polyorganosiloxanes have been described in detail in reviews and monographs, we shall not discuss them here[39].

The considerable development which has occurred recently in organoboron polymers is reflected in the review by Zamyatina and Bekasova[148]. Several thermostable polymers have been found among these compounds.

Bamford and Fordham [149] obtained polyesters of diboronic acids with tetrakishydroxyalkylated polymethylenediamines

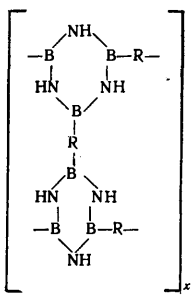


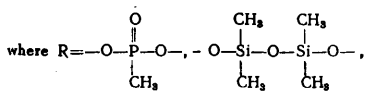
which were stable up to 300° and resistant to hydrolysis. The zinc and diethyltin salts of benzenediboronic acid are polymeric in character, and melt above 500°, as Korshak *et al.* [150] discovered. These workers also obtained polyaminoanhydrides of benzene-*p*-diboronic acid, which melt above 300° and have the structure



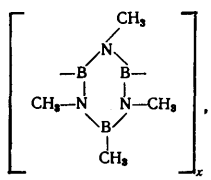
Polyesters of pentaerythritol and boric acid melt above 300°. [151]

Thermostable polymers containing borazole rings linked with residues of methylphosphonic acid or tetramethyldisiloxane

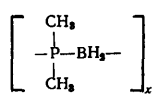




melting above 300°, were obtained by Korshak and his coworkers [150,152]. Eilar and Wagner [153] obtained a polymer comprising borazole rings

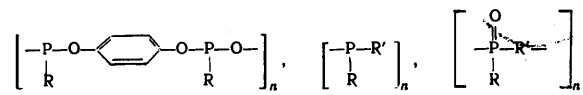


which is stable at 350–500°. Burg [154] prepared a phosphine–borane polymer of structure

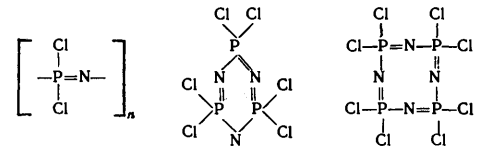


which was stable up to 400°.

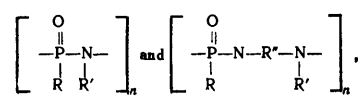
Let us discuss briefly polymers containing P–O and P–C bonds, for example [7]



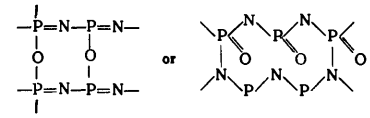
When R = R′ = phenyl, the polymers are stable in air at 300°. Their low molecular weight constitutes a disadvantage. When P is replaced by As, the stability of the polymers at 300° is preserved in a vacuum. Polymers containing P–N bonds exist in linear, trimeric, and tetrameric forms



On being heated to 300° the cyclic trimers are converted into a rubberlike mass having a linear structure. These polymers are unstable to hydrolysis. Polymers containing P–N bonds, obtained by the condensation of phosphorus chlorides with amino-compounds, of the type



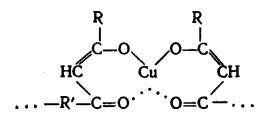
are stable up to 300°. Phosphoroxynitrides resemble ceramic materials [7]: they are stable over a wide range of temperatures, and above 1000° are converted into a glass. The disadvantage is that they are hydrolysed by water when heated above 200°. [7] They have the structure



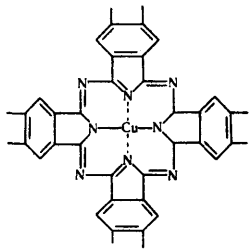
During recent years research has been carried on actively into the production of polymers containing boron–nitrogen bonds. A large number of such polymers have been obtained, their main defect being the comparative ease with which the B–N bonds are hydrolysed [147]. Polymers of this type containing borazole rings in the macromolecule are most interesting, as are also polymeric phosphine–boranes [7].

Coordinate bonds and bonds linking a metal with carbon in metallocene compounds can also be involved [155,156] in the formation of macromolecular organoelementary compounds containing various elements in the polymer chain.

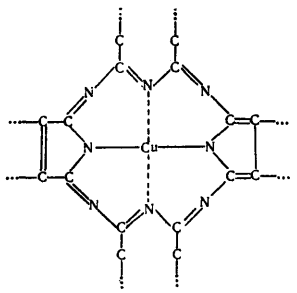
Many inner complex (chelate) polymers have been obtained of such metals as Cu, Be, Zn, Cd, Zr, Cr, Co, Ni, Fe, etc. [157-159]. As ligands linked with these metals various tetraketones have been widely used, yielding coordination polymers of the structure



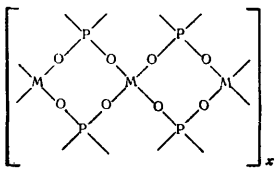
These are powders of various colours, decomposing at 250–400°; with the exception of the beryllium and zinc compounds [159], they are all insoluble. Phthalocyanine polymers of copper [160]



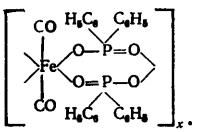
are very thermostable. Very interesting coordination polymers of copper and tetracyanoethylene, obtained by Berlin *et al.* [161], are infusible black powders of parquet structure



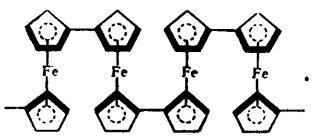
Interesting polymers of beryllium, zinc, copper, and chromium have been prepared by Block *et al.* [162] by the action of diphenylphosphinic acid on the metal salts. They have the structure



The beryllium, zinc, copper, chromium, and cobalt polymers decompose at 530°, 495°, 293°, 296°, and 400° respectively. Novel polymers have been obtained by Podall and Lapalucci [163] by the action of diphenylphosphinic acid on the carbonyls of chromium (decomp. temp. 360°) and iron (305°), which have the structure



Polyferrocenylene, which was prepared by Korshak *et al.* [151] by the polyrecombination of ferrocene, is a brown product melting at about 300° and having the structure



A large number of coordination polymers have been described in reviews by Berlin and Matveeva [157], Rode *et al.* [158], and other writers [38,122,159].

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The compounds discussed above by no means exhaust the possible types of thermostable polymers. Here we have given only a few examples illustrating the main routes used for the formation of thermostable polymers.

Immense opportunities for the synthesis of thermostable compounds, as yet undiscovered, are to be expected among inorganic polymers, which we have not discussed at all in this review, although several promising prospects in this interesting field are already beginning to appear [38].

By means of this review we have aimed to draw attention to this rapidly developing field, and to show that definite theoretical concepts have already been established to enable synthesis to be consciously directed towards the production of thermostable polymers.

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STRUCTURE AND PROPERTIES OF ORGANOPHOSPHORUS COMPOUNDS

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I. INTRODUCTION

The interest in organophosphorus compounds which has grown in recent years is explained by the considerable broadening of their field of use. Much attention has been paid to establishing the relation between the structure and properties of organophosphorus compounds, which is important, in particular, for solving the problems associated with the production of materials with specified properties.

Hammett's constant[1] is now widely used as a quantitative or semiquantitative characteristic of the structural features of organic compounds which determine their chemical and physical properties; it has been shown that the effect of *meta*- and *para*-substituents in the benzene ring on the rate constant or equilibrium constant of a reaction is expressed by the equation:

$$\log K - \log K_0 = \sigma\rho, \quad (1)$$

where K and K_0 are the rate or equilibrium constants of the reactions with the substituted and unsubstituted molecules respectively, σ is a constant characterising the polar effect of the substituent (the inductive effect and the conjugative effect), and ρ a constant characterising the reaction type and conditions.

Jaffé[2] has given evidence of the wide use of Hammett's equation; his review has values of σ and ρ for ~ 42 000 rate and equilibrium constants for 3180 reactions, which include addition, substitution, esterification, polymerisation, and copolymerisation. Eqn. (1) is satisfied with an accuracy of ±15% by experimentally measured rate or equilibrium constants of the reactions. This shows that although Hammett's equation does not give accurate results, it is sufficiently reliable for a first approximation.

Hammett's equation is applicable for benzene derivatives but inadequate for alkyl compounds. Furthermore, the constants σ are not always independent of the nature of the reaction. These constants reflect the polarisability of the bonds under the influence of the inductive effect and the conjugative effect, but it is known[3] that in the transition state the conjugative effect can vary according to the reaction type. Eqn.(1) does not take into account steric factors.

In this connection, Taft[4] proposed the empirical equation:

$$\log K - \log K_0 = \sigma^*\rho + E_s\delta + \psi^*, \quad (2)$$

for esterification, hydrolysis, alcoholysis, and various other exchange reactions, where K and K_0 are the rate or equilibrium constants for the substituted molecules and the molecules with the standard substituent CH_3, σ^* is the polarity constant of the substituent, E a constant characterising the steric effect of the substituent with respect to the CH_3 group (the standard), ψ a constant characterising the conjugative effect arising as a result of the interaction of the substituent and the reaction centre, and ρ and σ are constants which characterise the reaction type and conditions. This equation can eliminate the defects mentioned to some extent.

For hydrolysis, the polarity constant of the substituent is calculated by the formula:

$$\sigma^* = \frac{1}{2.48}\left[\log\left(\frac{K}{K_0}\right)_B - \log\left(\frac{K}{K_0}\right)_A\right], \quad (3)$$

where $(K/K_0)_B$ and $(K/K_0)_A$ are ratios of the constants of the reactions of alkaline and acid hydrolysis (under the conditions: the same ester, solvent, identical temperature), and 1/2.48 is a coefficient relating all the quantities to the Hammett scale.

It has been shown[3] that the Hammett and Taft equations are applicable to tautomeric equilibria and also to a series of exchange reactions, substitutions, and additions involving certain organophosphorus compounds. In addition to the quantitative and semiquantitative characteristics of the influence of the structural features of organophosphorus compounds on their reactivity and physical properties, there are works which characterise this effect without using empirical equations and constants.

In this article an attempt is made to review and systematise the available material on the study of the relation between the structure and the physical, and chemical properties of organophosphorus compounds.

II. REACTIVITY OF ORGANOPHOSPHORUS COMPOUNDS

1. Substitution, Addition, Hydrolysis, and Isomerisation; Tautomeric Equilibrium

A series of investigators[5-10] has established a relationship between the Hammett and Taft constants and rate constants of the reactions of certain organophosphorus compounds.

A relation has been found between the dissociation constant and the basicity index pK_a of phosphines and the Taft constants[11] $\Sigma\sigma^*$ characterising the polarity of the substituents $\Sigma\sigma^* pK_a = -\log K_a$, where K_a is the dissociation constant of the acid. This dependence is reflected in Tables

1 and 2, which show that the basicity of the phosphines decreases with increase in the polarity, so that there is consequently also a decrease in their reactivity in substitutions and additions. There are departures from the general rule, for example, for $(C_2H_5)_3P$ $\Sigma\sigma^* = -0.3$, $pK_a = 8.69$; and for $(^iC_4H_9)_3P$ $\Sigma\sigma^* = -0.375$, $pK_a = 7.97$.

The possibility of using the Taft constant for the reaction of phosphines with alkyl halides has been demonstrated[12]:

$$RR'R''P + C_2H_5I \xrightarrow[\text{acetone, } 35^\circ]{K_2} RR'R''C_2H_5P^+ + I^-.$$

With increase in the polarity in the alkylphosphine series, their reactivity increases in the following order:

$$C_2H_5P(CH_3)_2 > (C_2H_5)_2PCH_3 > (CH_3)_3P > (C_2H_5)_3P;$$

trimethylphosphine is anomalous. As a rule there is a decrease in the rate constant of this reaction with increase in the polarity, according to the equation

$$\log 10^5 K = 1.939 - 0.767\sigma^*. \quad (4)$$

In this it is assumed that other factors (steric and conjugative) have little effect on the rate constants of phosphine reactions[12].

In a study[13] of substitution at phosphorus(V) it was noted that nucleophilic substitution at phosphorus depends on the relative magnitude of the polarity and polarisability of the phosphorus compound (the $-\overset{|}{\underset{|}{P}}=O$ group has a marked influence) and on the relative magnitudes of these properties of the nucleophilic reagent.

The polarisability of the phosphoryl group is greater than that of the carbonyl, and therefore a greater inductive effect is possible in phosphorus compounds than for their carbon analogues. Allowance must be made for the possibility of the double bond in phosphorus compounds being formed with *s*, *p*, and *d* orbitals[14], whereas in carbon compounds a double bond is formed by electrons of *s* and *p* orbitals.

A nucleophilic substitution which has been studied more fully is the hydrolysis of organophosphorus compounds, which is catalysed by both hydrogen and hydroxide ions[5].

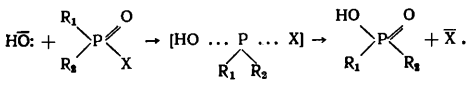
TABLE 1. Equations relating basicity and the Taft constant $\Sigma\sigma^*$ of alkyl- and aryl-phosphines[11].

Compound	Equation	Compound	Equation
Phosphines:		Amines:	
tertiary	$pK_a = 7.85 - 2.67\ \Sigma\sigma^*$	tertiary	$pK_a = 9.61 - 3.3\ \Sigma\sigma^*$
secondary	$pK_a = 5.13 - 2.61\ \Sigma\sigma^*$	secondary	$pK_a = 12.13 - 3.23\ \Sigma\sigma^*$
primary	$pK_a = 2.46 - 2.64\ \Sigma\sigma^*$	primary	$pK_a = 13.23 - 3.14\ \Sigma\sigma^*$

TABLE 2. Values of pK_a and $\Sigma\sigma^*$ for various phosphines[11].

Compound	$\Sigma\sigma^*$	pK_a	Compound	$\Sigma\sigma^*$	pK_a
Tertiary phosphines:					
$(CH_3)_3P$	0.00	8.65	Secondary phosphines:		
$C_2H_5P(CH_3)_2$	−0.10	8.62	$(C_2H_5)_2PH$	1.69	0.03
$(C_2H_5)_2PCH_3$	−0.20	8.62	$(CNC_2H_4)_2PH$	2.09	0.41
$(C_2H_5)_3P$	−0.30	8.69			
$(^iC_4H_9)_3P$	−0.375	7.97			
$(C_2H_5)_2PC_6H_5$	+0.40	6.25			
$(C_6H_5)_3P$	+1.8	2.75	Primary phosphines:		
			$^nC_6H_{17}PH_2$	0.85	0.43
			PH_3	1.47	14

The most extensive investigation has concerned alkaline hydrolysis, for which the following scheme has been proposed:



The effect of the nature of the substituents on hydrolysis rate was studied[6]; replacement of alkyl by alkoxy usually leads to a decrease in hydrolysis rate.

Kabachnik[3] examined the data on the alkaline hydrolysis of alkyl alkylphosphonofluoridates and on the alcoholic solvolysis of dialkyl phosphorochloridates, using the constant σ (Figs. 1 and 2). Some breakdown in the proportionality between Hammett's constants and the reaction rate is possible because there are two opposing effects. On the one hand the increase in the charge on the phosphorus accelerates the reaction, and on the other this increases the increment of the energy of conjugation of the P–O bond, which leads to a decrease in reactivity[7]. Therefore replacement of an ethoxy-group by a phenoxy-group causes an increase in the hydrolysis rate. pH has a very strong influence on the rate of reaction; thus, the reactivity of monoalkyl phosphates is greatly increased at pH 1–5.[8] In acid media the rate of hydrolysis increases with the polarity of the substituent, and in alkaline, hydrolysis is possible at the C≡N bond as well as at the C–O–P bond[9].

As well as the polarity constants of the substituents, their steric characteristics must also be taken into account. Thus the steric hindrance of the substituent $CH_3NHCH_2CH_2-$ is less than that of the substituent $(C_2H_5)_2NCH_2CH_2-$ by a factor[4] of ~ 3.5.

The reaction rate also depends on the solvent. For example, as the basicity of the solvent is increased the P–X bond energy decreases, but simultaneously there is an increase in the steric hindrance (Table 3).

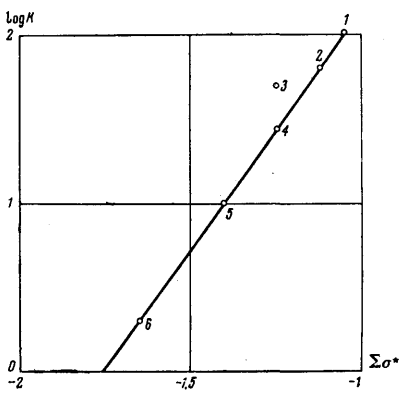


Fig. 1. Dependence of $\log K_1$ on $\Sigma\sigma^*$ for the alkaline hydrolysis of esters of alkylphosphonofluoridic acids:
1) $CH_3P(O)(OCH_3)F$;
2) $CH_3P(O)(OC_2H_5)F$;
3) $CH_3P(O)(OC_3H_7)F$;
4) $CH_3P(O)(O^iC_3H_7)F$;
5) $C_2H_5P(O)(O^iC_3H_7)F$;
6) $C_3H_7P(O)(O^iC_3H_7)F$.

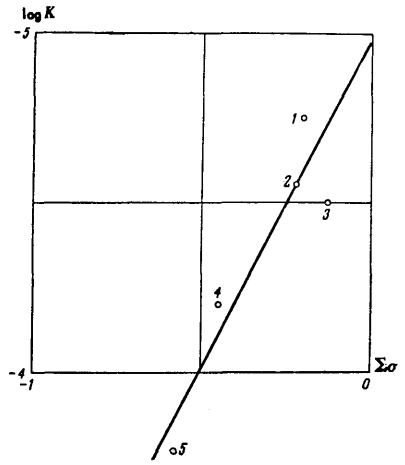


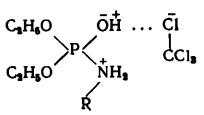
Fig. 2. Dependence of $\log K_1$ on $\Sigma\sigma$ for the solvolysis of dialkyl phosphorochloridates by alcohol: 1) $(CH_3O)_2POCl$; 2) $(C_6H_5CH_2O)_2POCl$; 3) $(C_6H_5O)_2POCl$; 4) $(C_2H_5O)_2POCl$; 5) $(^iC_3H_7O)_2POCl$.

TABLE 3. Dependence of the rate constants for the hydrolysis of acid chlorides of phosphonic acids ($10^3 K$) on the nature of the solvent[7].

Solvent	σ^* of substituent at OH group	10^3K at 25°***	E_{act}*	log A**
H—(OH)	0.49	128	8.5	5.37
CH_3—(OH)	0.00	10.3	8.0	3.88
C_2H_5—(OH)	—0.10	5.7	7.3	3.07

* Energy of activation.
** Activity constant of the solvent.
*** The last entry in this column should be 5.07 according to the original; log A is really the log of the Arrhenius factor, PZ (Ed. of Translation).

In several instances the solvent has quite a strong influence on the reactivity of phosphorus-containing compounds, which is explained by the formation of an intermediate compound, for example, in the reaction of phosphites with amines in the presence of polyhalides[10]:



The replacement of CCl_4 by CCl_3Br or $CNCCl_3$ increases the reactivity of phosphorus-containing compounds of phosphites [*sic* (Ed. of Translation)].

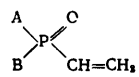
In addition to the hydrolysis and solvolysis of various phosphorus-containing compounds, there have been investigations of the alkaline cleavage of phosphonium salts, the protolysis of phosphorus acids, and of benzylation[15-17]; Hammett's equation is applicable to all these reactions.

Several papers[18-24] have established a correlation between the dissociation constants of phosphonic acids or their derivatives and the Hammett constants. A linear relation between σ and pK_a is obtained for aromatic phosphonic acids[18,19]. The Taft constants were also determined for the reaction of hydroxamic acids with phosphonofluoridates[20-24].

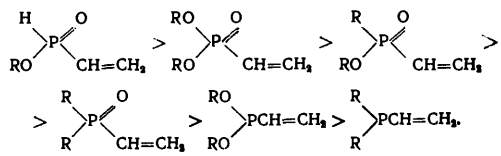
Since the tautomeric equilibrium constant in the selected medium equals the ratio of the ionisation constants of the tautomeric forms, which, in turn, can be calculated by Hammett's equation[1,3], the equilibrium position is mainly determined by the magnitude of Hammett's constant, characterising the nature of the substituent. Kabachnik showed the applicability of Hammett's equation to the tautomeric equilibrium of phosphorus thio-acids[22-24]:

$$(RO)_2P(S)OH \rightleftarrows (RO)_2P(O)SH,$$
$$R(RO)P(S)OH \rightleftarrows R(RO)P(O)SH, \text{ etc.}$$

Study of the bromination of unsaturated phosphorus-containing compounds and their addition to secondary amines shows that Hammett's equation is also applicable to these reactions[3,25]. As the value of $\Sigma\sigma$ of the substituents is reduced, the reactivity of the vinyl group in compounds of the type



also decreases. For such compounds, and also for analogous compounds of phosphorus(III), a series of decreasing reactivity of the vinyl group has been compiled[25]:



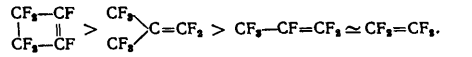
For the first four compounds of this series ($R = -C_4H_9$), $\Sigma\sigma$ is respectively -0.411, -0.822, -1.370, and -2.438.

In addition to those mentioned there are several investigations which establish a qualitative relation between the reaction rate and the structure of the reactants. Thus, the addition of phosphines to unsaturated compounds of the styrene type has been studied[26,27]. Phosphines are chain carriers in polymerisation:

$$RPH + CH_2{=}CHX \rightarrow RPHCH_2{-}\dot{C}HX + RPH_2 \rightarrow RPHCH_2CH_2X + R\dot{P}H,$$

where $R\dot{P}H$ is the chain carrier.

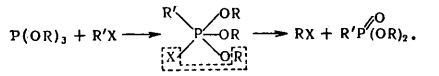
For the addition of phosphines to the vinyl group the substituent R in the phosphines can be arranged in the following series of decreasing activity[27]: bis-(2-cyanoethyl) > > 2-cyanoethyl > phenyl > octyl. The addition of phosphorus-containing compounds to unsaturated bonds of a monomer depends on the structure of the monomer containing this bond. Thus the activity of perfluoroalkenes in the reaction with triethyl phosphite falls in the sequence[28]:



Many investigators[29-48] have evaluated the reactivity or the activity of a compound by the yield of the main product and the time of reaction.

In particular it has been noted that the Arbuzov rearrangement proceeds more rapidly and with a greater yield the more electronegative and the smaller the radical in the alkyl

halide [37-45]. Thus, rearrangement does not occur with 9-chloroanthracene but does with 9-chloroacridine [43]. Polymerisation proceeds through intermediate addition products [33]:



Radicals entering into the composition of phosphite esters also affect the isomerisation rate: the rate is greater with radicals of small dimension and high electronegativity. According to their influence on reaction rate, the groups attached to phosphorus can be arranged in the series [32,33]: Alk > Ar > AlkO and $CH_3O > C_2H_5O > C_3H_7O > C_4H_9O$.

Other conditions being equal, the rate of isomerisation of phosphite esters depends on the halogen of the alkyl halide [33,46]. The reaction under the action of alkyl iodides is more rapid than that with the chlorides; bromides occupy an intermediate position.

Thus, for several exchange reactions, substitutions, additions, isomerisations, and tautomeric equilibria of phosphorus-containing compounds the Taft constants can be used for the quantitative or qualitative characterisation of the reactivity of the reactants.

2. Polymerisation, Copolymerisation, and Telomerisation

The applicability of Hammett's equation has been shown for the polymerisation and copolymerisation of common organic compounds, but such investigations of the polymerisation of phosphorus-containing monomers have not been made [47,48].

The polymerisation and copolymerisation of phosphorus-containing unsaturated compounds of various structures has been studied without using Hammett's and Taft's constants. Toy and Cooper [49] give the comparative characteristics of phosphorus-containing monomers for activity in polymerisation, by the example of diallyl alkylphosphonates, where we will quote the R in $RP(O)(OCH_2CH{=}CH_2)_2$:

$$C_6H_5{\simeq}H > C_6H_5CH_3 \simeq C_6H_5O \simeq (CH_2)_2C{=}CH_2 \gg C_6H_5CH{=}CH > > CH_3 \simeq C_2H_5 > {}^iC_3H_7 \simeq C_8H_{17} \gg C_2H_5O \simeq (CH_2)_2N.$$

Kamai and Kukhtin [50] gave the following series:

$$C_6H_5 > RC(=O) > ROC(=O) > ROCCH_2(=O) > CCl_3 > CH_3 > C_2H_5.$$

Kennedy and coworkers [51] supplemented and corrected these two series for allyl alkylphosphonates, and gave this series for the activity:

$$CCl_3 \simeq CCl_2{=}CHO \gg H \gg CH_2{=}CHCH_2O \simeq OCH_3 \simeq C_2H_5OCCH_2(=O) > > CH_3{=}CHCH_2 \gg OH \simeq N(CH_2)_2 \simeq CH[N(C_2H_5)_2]CH{=}CH_2. \quad (I)$$

The series of compounds $A_3P{=}O$, $(AO)_2P(O)OH$, $(AO)_2P(O)N(CH_3)_2$, $(AO)_2P(O)CH(NEt_2).CH:CH_2$, and $(AO)_3P$ (A = allyl group) do not form solid polymers, and the last three of this series even inhibit polymerisation.

These series suggest that the greater the electronegativity and the smaller the substituent at the phosphorus atom in the allyl esters, the more readily polymerisation takes place.

When there is little interaction between the π electrons of the allyl group and the P=O bond, for example, in the compounds $(CH_2{=}CHCH_2)_3PO$ and $(CH_2{=}CHCH_2)_2P(O)OH$, the ability to polymerise is negligible [51] These results have been repeatedly confirmed [52-61], but several results have been obtained which do not correspond with the empirical series [50,51,53,54]. This is because the polymerisation rate can be strongly depressed by impurities in the monomers [51,53,54]. The presence of even insignificant amounts of triallyl phosphite completely inhibits polymerisation [51].

Upson, Kabachnik, Gefter, and many other investigators [62-78] have studied the ability of phosphorus compounds with a vinyl group to polymerise. Unlike allyl esters — whose activity in the presence of three double bonds (three allyl groups) in polymerisation is small — the analogous vinyl esters readily form solid vitreous polymers [62].

Vinyl esters with one double bond either do not polymerise at all, or form viscous liquids or gelatinous polymers, depending on the substituents at the phosphorus atom.

The preparation and polymerisation of derivatives of vinylphosphonic acids have been studied [65-77]; usually, the larger the aliphatic radical in the ester group, the lower the molecular weight of the polymers obtained but the greater the yield of phosphorus-containing polymer [66]. Fig. 3 shows the results of the polymerisation of vinylphosphonic esters of various structures.

The polymerisation of unsaturated derivatives of phosphorus acids has formed the subject of many papers. Polymers have been obtained from $(HOCH_2)_4PR$, where R is the residue of an unsaturated acid (methacrylic or acrylic), from various phosphorus-containing dienes, vinylphosphine oxides [74-76], etc. Vinylphosphine oxides polymerise very badly, which some investigators attribute to the large steric hindrance [76]. Products of higher molecular weight are obtained from monovinylphosphine oxides on irradiation with X-rays [76].

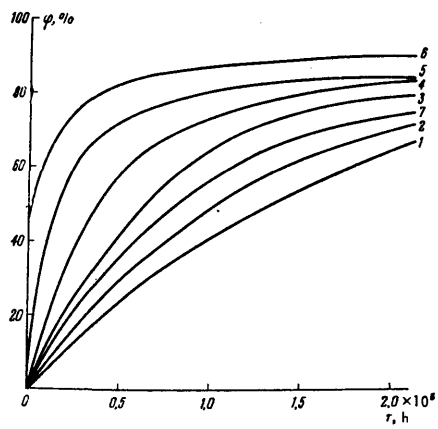


Fig. 3. [Polymerisation of vinyl phosphonic esters of various structures (Ed. of Translation).]* Dependence of the yield of polymer φ on the duration of the reaction: 1) ethyl and isopropyl esters; 2) n-propyl ester; 3) methyl ester; 4) n-butyl and isopentyl esters; 5) n-hexyl ester; 6) n-heptyl ester; 7) isobutyl ester.

* Since 2×10^5 h is about 20 years it is likely that the time scale should be 10^{-5} t where t is in seconds (Ed. of Translation).

There is considerable interest in the study of the relation between the structure of phosphorus-containing monomers and their activity in copolymerisation [79-100]. The copolymerisation of styrene and diethyl vinylphosphonate has been studied. Arcus and Matthews[98] found the constants for the copolymerisation to be $r_1 = 3.25$; $r_2 = 0$.

The copolymerisation of acrylonitrile and esters of vinylphosphonates has also been studied[66]; Table 4 shows that the activity of the esters increases with decrease in the polarity and increase in the length of the ester residue: the polarity of the methyl, ethyl, isobutyl, and n-butyl radicals are respectively $\sigma_1 = 0.00$, $\sigma_2 = -0.100$, $\sigma_3 = -0.125$, $\sigma_4 = -0.130$.

The copolymerisation of acid chlorides of unsaturated phosphorus acids with vinyl monomers [80,90], of vinyl monomers with unsaturated phosphorus-containing polyesters, and of phosphorus-containing monomers with unsaturated polyesters [89-95] has been studied.

Polymers can be obtained by addition of phosphines to the double bond of a polyester or monomer. Phosphonates can be used instead of the phosphines [80,101]. The rate of this copolymerisation depends on the initiation conditions [80,101]. A high activation energy ensures sources of free radicals or conditions which guarantee the formation of free radicals. In several instances, for example, in the copolymerisation of styrene with a phosphorus-containing polyester, an accelerator of the reaction (here, isocyanates) is used to increase the rate of reaction [102]. The copolymerisation of *p*-xylylenes with phosphorus trichloride gave thermostable polymers [103,104].

The telomerisation of unsaturated phosphorus-containing compounds has been studied [105-107]. It has been established that trialkyl phosphites can undergo the Arbuzov rearrangement under the action of $\alpha\beta$-unsaturated aldehydes and acids. It is suggested that in the case of the acids telomerisation is possible, the reaction proceeding thus:

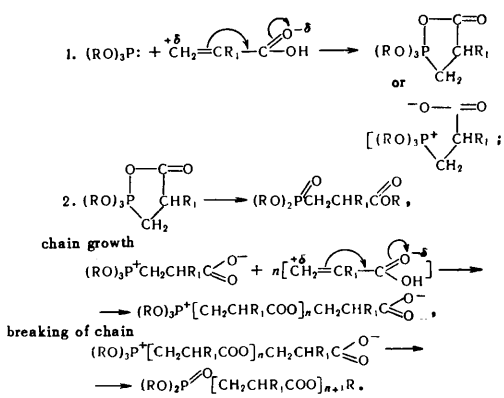


TABLE 4. Copolymerisation of vinylphosphonate esters with acrylonitrile[66].

Ester	σ^* of substituent in RO	E_s of substituent in RO	Composition of initial mixture, %		Yield of copolymer, %	Composition of copolymer, %	
			acrylonitrile	ester		acrylonitrile	ester
Methyl	0.00	0.00	50	50	18	86.5	13.5
Ethyl	−0.10	−0.07	55.7	44.3	33.3	82.4	17.6
Isobutyl	−0.125	−0.93	58.5	41.5	25.6	78.7	21.3
n-Butyl	−0.130	−0.39	50	50	37.3	63.1	36.9

The authors of this investigation suggest that during the reaction an intermediate dipolar ion is formed and further reaction can proceed in two directions: the Arbuzov rearrangement or telomerisation [106].

Telomers can be formed in the reaction of alkenes with phosphorus acid:

$$RCH{=}CH_2 + H_3PO_2 \xrightarrow[\text{ultraviolet}]{\text{peroxides}} RCH_2CH_2CHR\,P(O)(OH)_2 \text{ (product I)} +$$

$$+ RCH_2CH_2P(O)(OH)_2 \text{ (product II)}.$$

The percentage yield in this reaction depends on the structure of the alkene and is determined by the nature of the radical [107]:

R	Yield of I	Yield of II	Total yield
$^nC_4H_9$	8	23	31
C_6H_{11}	9	20	29
$^nC_8H_{17}$	6	18	24

From the above, it is evident that as the size of the substituent is increased, the total yield of the products diminishes. Hence, for polymerisation, copolymerisation, and some telomerisations we can compile series for the influence of the substituents on the rate of reaction or the activities of the reagents. The substituents are arranged according to their electronegativity and dimensions.

3. Polycondensation

Of the polycondensation phosphorus-containing resins, the best known are the phoryl resins of type $[OArOP(O)(OR)]_n$, which were obtained earlier [108] from phosphoryl chloride and polyhydric phenols. Subsequently analogous resins were made in which alkyl (or aryl) is attached directly to a phosphorus atom, from acid chlorides of phosphorus acids and polyhydric phenols or other compounds containing two or three hydroxyl groups. For example [110]:

$$n\,ClP(O)Cl + n\,HOROH \rightarrow [-P(O)ORO]_n + n\,HCl,$$

where R′ is CH_3, and

$$R{-}O{-}C_6H_4{-}O{-}\text{, }{-}O{-}(CH_2)_n{-}O{-}\ (n = 2, 4, 6),\ \text{or}\ {-}O{-}[(CH_2)O]_n{-}\ (n = 2, 3).$$

In such a reaction the components are rapidly exhausted — after 4 h, 95% of the reactants have been consumed.

In carrying out polycondensations under ordinary conditions using methyl-, chloromethyl-, or phenyl-phosphonic dichlorides and hydroquinone as reagents, the reaction was less complete when the phenylphosphonic dichloride was used, which may be due to a steric effect of the substituent on the reaction rate. The degree of completion of the reaction also falls with an increase in the length of the alkyl group up to heptyl [111]. When the acid dichlorides react with glycols, especially with glycols having from 2 to 4 carbon atoms, cyclic esters are formed, which sensibly reduces the yield of polyester [111,112]. The reaction conditions, especially temperature and duration, have a marked effect on the rate of polycondensation (Figs. 4 and 5) [109-111].

By carrying out the polycondensation at high temperature or on heating in a vacuum, polymers could be obtained from dichloroethyl alkyl- and aryl-phosphonates, and also

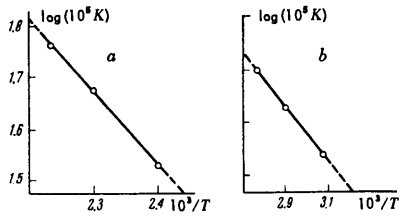


Fig. 4. Temperature dependence of the rate constants of the reaction of methylphosphonyl dichloride with: *a*) hydroquinone; *b*) diethylene glycol.

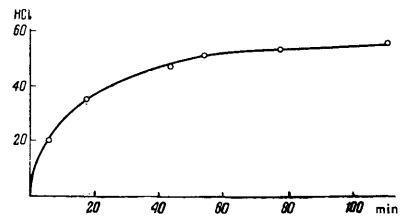


Fig. 5. Rate of liberation of HCl with time in the reaction of phenylphosphonyl dichloride with hydroquinone at 91°, with $MgCl_2$ catalyst. [The graph appears to give the total HCl liberated with time rather than the rate of liberation of HCl with time (Ed. of Translation).]

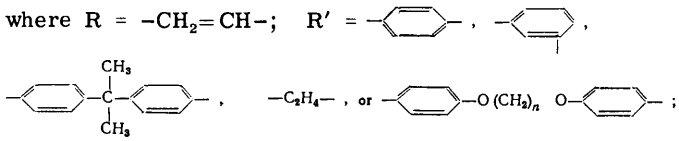
from phosphorus esters of the type $ClCH_2C_6H_4P(OR)_2$.[113-115] In investigating the polycondensation of di-2-chloroethyl methylphosphonate it was noted that an increase in the duration of the reaction brings about an increase in the yield of products of low molecular weight. It was also found that the yield of the polymer depends on the nature of the substituent and the temperature of the reaction. During the reaction[114,115]:

$$n\,ClCH_2C_6H_4P(OR)_2 \rightarrow -[-CH_2PC_6H_4CH_2-]_n- + RCl,$$
(O; OR)

the alkyl halide is released and the reaction mechanism is similar to that of the Arbuzov isomerisation.

Resins of type $-[-(R)P(O)OR'O-]_n-$ can be obtained by polymerisation[91,93-95,116,117]:

$$n\,RP(O)(OR'')_2 + n\,HOR'OH \rightarrow -[-(R)P(O)OR'O]_n + R''OH,$$

where R = $-CH_2=CH-$; R′ = 

R′ = C_2H_5 or C_6H_5.

This reaction is carried out in the presence of catalysts — magnesium chloride or zinc acetate — at temperatures up to 250°. The reaction rate is greater with diphenyl vinylphosphonate than with the diethyl ester, but the yield of polyester is rather greater in the reaction of diphenyl vinylphosphonate with hydroquinone and diphenylpolypropane than with resorcinol. A change in the structure of the dihydroxy-compound has very little effect on the yield of polymer[91].

Ethylenepolyphosphites $[O(CH_2)_mOP(OH)]_n$ were obtained by poly(ester interchange), and polyesterification was used to give poly(phosphorus esters), polymers based on $(RCH_2)_2P(O)CH_2OCH_2CH(OH)R'$ [117,118] and various others. However, the activity of the monomers in these reactions in relation to their substituents has still not been studied.

There is considerable interest in studying the reaction of di(alkoxycarbonylaryl)phosphine oxides† with various diamines and hydroxy-compounds, and also in making polyphosphonamides[119-124]. The latter can be obtained thus:

$$C_6H_5P(O)(NH_2)_2 \xrightarrow{-NH_3} -(-P(O)(C_6H_5)-NH-)_n.$$

The structure of the polymer depends on the reaction temperature. Thus up to 275° polymers are obtained with molecular weight averaging from 300 to 400, which is explained by the formation of a cyclic dimer or trimer; above 300° polymers of higher molecular weight are obtained. Below 200° polycondensation products are not formed[122]. Polymers with P–N-type bonds

$$-[-P(O)(C_6H_5)N(CH_3)-]_n-,\quad -[-P(O)(NH_2)-NH-]_n-,\quad -[-P(O)(C_6H_5)-NHCONH-]_n-,\quad -[-P(O)(C_6H_5)-NHCSNH-]_n-$$

were obtained respectively from substituted phenylphosphonium diamines, $POCl_3$ and NH_3, phenylphosphonic diamides, and urea or thiourea[122-124]. Similar polymers can be obtained from nitrogenous compounds and phosphorus-containing acid dichlorides. Various polymers have been obtained using these acids and tetrahydroxymethylphosphonium derivatives[125-136].

III. PROPERTIES OF ORGANOPHOSPHORUS COMPOUNDS

1. Low-Molecular-Weight Compounds

Physical properties are known to be related to the chemical ones, since both depend on the structure of the compound. And since reactivity can be evaluated by empirical quantities which quantitatively or semiquantitatively characterise the structural features of the compound, then it is natural for these quantities and the physical properties to show a relationship[137-141].

Thus, for organophosphorus compounds there is a quantitative relation between the displacement of the $-P(=O)-$ bond frequency (γ_{PO}) and the Taft constants $\Sigma\sigma^*$, which can be expressed by the equation[137]:

$$\gamma_{PO} = 16.8\Sigma\sigma^* + 1198. \qquad (5)$$

Usually the values of γ_{PO} calculated by Eqn. (5) and found experimentally agree or are very close. The value of

† For example $(MeO_2C.C_6H_4)_2P(O)Et$ (Ed. of Translation).

γ_{PO} increases with the polarity of the substituent in phosphorus(V) compounds. As the steric hindrance increases it becomes necessary to introduce a correction into the value of E_S. Subsequent work has shown a linear relation between the absorption frequency of various bonds and the total inductive effect of the substituent groups[141].

In studying the nuclear quadrupolar resonance spectra of phosphorus compounds, in particular phosphoryl chloride and phosphorus trichloride, it is found that conjugation can be transmitted through the phosphorus(V) atoms. Furthermore, a relation has been reported between the electronegativity of the substituent and the resonance frequencies for the compounds $RP(O)Cl_2$.[142]

A relation is observed between the Taft constants and such physical properties as boiling and melting points, refractive indices, and density.

Table 5 shows the Taft constants and data on some physical properties of various organophosphorus compounds. Usually the melting or boiling points and refractive indices of these compounds increase with the polarity (σ^*) and with a decrease in steric hindrance E.

A change in the radical of the ester group at the phosphorus atom leads to the reverse dependence between polarity, the steric factors of the substituent, and the physical properties, which is characteristic for aliphatic radicals. Table 6 shows such results for phosphonic esters and phosphorodichloridates, together with the corresponding Taft constants and the physical properties of phosphoric acid derivatives containing aryl radicals in the ester group. In this case there is a linear relation between the polarity of the radical and the boiling point of the compound[143-150].

The relation between the nature of the substituent and the physical properties of the compound has been studied by other investigators[150-153] also. Despite individual exceptions it can be concluded that there is a connection between the nature of the substituent, which is characterised by the empirical quantities, and the physical properties of organophosphorus compounds containing this substituent.

TABLE 5. Taft constants for substituents of a series of phosphorus-containing compounds and their physical properties[108].

Compound	σ^*	E_S	Boiling point, °C/mmHg	Melting point, °C	Refractive index
$RP(O)(OR')_2$					
R:					
C_2H_5	−0.10	−0.07	53/30		1.422
$C_6H_5CH_2$	+0.215	−0.38	88—90/3		1.503
C_6H_5	+0.60		100/5		1.513
$ArPCl_2$					
p-$CH_3C_6H_4$	+0.6		109—110/11		
p-ClC_6H_4	+1.00		132—133/20		
m-ClC_6H_4	+1.04		124—125/18		
p-CNC_6H_4	+1.228		127—128/4.5		
$ArP(O)(OH)H$					
m-ClC_6H_4	1.04			90.9—91.5	
p-CNC_6H_4	1.23			166—167	
$ArP(O)(OH)_2$					
p-$Cl(CH_2)_3C_6H_4$	0.985			137	
CH_2-CHC_6H_4	1.00			173—174	
$R(OH)P(O)CH_2CH_2CH(NH_2)COH$					
C_6H_5	−0.1	−0.07		185—187	
C_6H_5	+0.6			237	
$RP(O)Cl_2$					
1) $ClCH_2$	1.05	−0.24	77—78/10		1.4978
2) CH_3CCl_2	$\sigma_1^* < \sigma_2^*$			147—150	
C_5H_{11}	−0.17	−0.4	64—69/2		1.4694
C_6H_5	0.6		104/4		1.5581
3) $C_6H_5CH_2$	0.215	−0.38	130/2	57.5	
4) C_6H_5CHCl	$\sigma_3^* < \sigma_4^*$		124/2	61	1.566
p-$CH_3OC_6H_4$	0.5		173/12		
p-$CH_3C_6H_4$	0.6		142/11		
$RP(O)(ArCOOH)_2$					
CH_3	0.00			285	
C_2H_5	−0.10			265	
C_6H_5	0.6			304—310	

TABLE 6. Taft constants for substituents in the ester group of a series of phosphorus-containing compounds and their physical properties[108,144-146].

Compound	σ^*	E_S	Boiling point, °C/mmHg	Refractive index
$CH_3P(O)(OR)(OR')$				
$R'=C_6H_5$	−0.10	−0.07	82—83/25	1.4265
C_3H_7	−0.115	−0.36	79/8	1.422
C_4H_9	−0.13	−0.39	96/3.5	1.43
$CH_3C(O)P(O)(OR)(OR')$				
$R'=C_2H_5$	−0.10	−0.07	76.5/2	1.435
C_3H_7	−0.115	−0.36	67/1	1.436
$ROP(O)Cl_2$				
CH_3	0.00	0.00	49	
C_2H_5	−0.10	−0.07	58	
C_3H_7	−0.115	−0.36	72	
C_4H_9	−0.13	−0.39	84	
C_6H_5	+0.6	—	104/2	1.522
p-ClC_6H_4	1.00	—	130/7	1.538
2,4,6-$Cl_3C_6H_2$	1.54	—	75 *	
2,4,6-$(CH_3)Cl_2C_6H_2$	1.14	—	57 *	

* Melting point, °C.

2. High-Molecular-Weight Compounds Obtained by Polymerisation

It is known that the presence in the polymer of a certain percentage of phosphorus brings about the appearance of self-extinguishing properties[49]. Thus, as the phosphorus content of poly(vinyl alcohol) fibres is increased, the flame resistance‡ of the fibre increases and the strength decreases. Table 7 gives data on the phosphorylation of poly(vinyl alcohol) fibres[154]. However, the flame resistance and the other physical properties of polymers depend not only on the phosphorus concentration but also on the nature of the substituent at the phosphorus atom. The structure of the polymers is determined by the structure of the monomers from which they are obtained. Therefore there is a definite correlation between certain physical properties of the monomer and of the polymer. For example, there is a relation between the thermal stability of the monomer and the flame resistance of the polymer[49]. With an increase in the former there is an increase in the latter. The flame resistance of polymeric phosphonates is greater than that of

TABLE 7. Comparison of the physical properties and phosphorus concentration of various fibres[154].

Fibre	P in fibre, %	Strength, r.km*	Elongation, %	Flame resistance	Colour
Ordinary	—	21.6	39	burns	pale yellow
Phosphorylated	1.94	16.1	43	burns 1 s, does not smoulder	yellow
Phosphorylated	6.02	14.7	67	does not burn, does not smoulder	dark brick red

* *Sic*; presumably an error. In the U.K., fibre strengths are normally expressed in g per denier (Ed. of Translation).

‡ Toy and Cooper's terminology.

polymeric phosphates (Table 8), mainly due to the greater stability of the P–C bond compared with that of the P–O–C bond [49,54].

Table 8 shows that the flame resistance of polymeric aromatic phosphonates is better than that of aliphatic ones despite a lower phosphorus content. Furthermore, such physical properties as melting point [57,59], softening point [66], and glass point [66] vary with the structure of the polymers. It has been noted that the glass points of polymers obtained on the basis of vinylphosphonate esters falls with increase in the length of the n-alkyl radical, but increases slightly with branching of the alkyl radical [66,68].

Fig. 6 shows the glass points of polymers obtained from vinylphosphonate esters as a function of the number of carbon atoms in the alkyl radical chain. The increase in the glass point can evidently be explained by an increase in the polarity of the radicals as the number of carbon atoms in the chain is reduced: $\sigma^*_{CH_3} = 0.00$, $\sigma^*_{C_2H_5} = -0.10$, $\sigma^*_{C_3H_7} = -0.115$, $\sigma^*_{C_4H_9} = -0.130$. Polymers are known which are obtained from methylphosphonic and vinylphosphonic dichlorides and diethylene glycol. Polyesters were obtained by polycondensations and were then polymerised at the vinyl groups. The softening point of these polymers increases with the concentration of vinyl groups in the polyester. Copolymers based on vinylphosphonic esters and various monomers, for example, acrylonitrile, have been obtained; their glass temperatures lie between 90° and 100°, [66] owing to the presence of the second component (acrylonitrile) in the copolymer.

Of the copolymers obtained from polybutyleneglycol fumarate and allyl phosphonates those with composition close to azeotropic have the best mechanical and dielectric properties [93,94]. The composition of the copolymers approximates to azeotropic in the region of relatively high polyester : monomer molar ratios (10 : 1). [92–95]

The thermal stability of the allyl alkylphosphonate copolymers depends on the alkyl group and on the ratio of the components in the reacting mass [108]. The relation between the polar§ factor of the substituent in the vinyl monomer and the softening point of the copolymer is shown in Table 9. In the copolymerisation of unsaturated phosphorus-containing polyesters with vinyl monomers [94] both the nature of the polyester and the vinyl monomer greatly influence the properties of the copolymer obtained. There is a sharp increase in the softening point when the polyester is obtained from an unsaturated phosphorus-containing acid and aromatic dihydroxy-compounds. However, when there is alternation in the polyester of aromatic bridges or groupings of the type $-Ar(CH_3)C(CH_3)Ar-$ it is necessary to allow for the steric factor of the substituent [80].

TABLE 8. Structure and flame resistance of phosphorus-containing polymers [49].

Monomer	Flame resistance of polymer	Phosphorus in polymer, %
$C_6H_5P(O)(OCH_2CH=CH_2)_2$	good	13
$CH_3P(O)(OCH_2CH=CH_2)_2$	good	17.6
$i\text{-}C_4H_7P(O)(OCH_2CH=CH_2)_2$	satisfactory	14.4
$P(O)(OCH_2CH=CH_2)_3$	bad (burns)	14.2
$HP(O)(OCH_2CH=CH_2)_2$	very bad (burns)	19.2

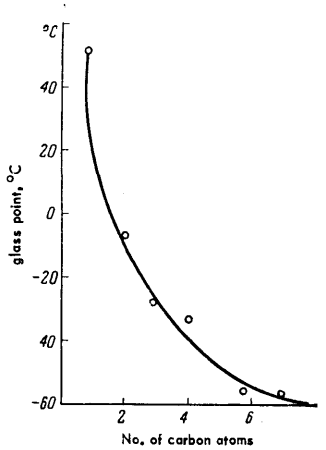


Fig. 6. Dependence of the glass point on the number of carbon atoms in the chain of the alkyl radical.

3. High-Molecular-Weight Compounds Obtained by Polycondensation

Attempts have been made to make a comparative appraisal of the dependence of polymer properties on structure for certain phosphorus-containing polymers obtained by polycondensations. Many investigators note [108,121,150,151,154,157,158] that replacement of a P–C bond by P–O–C in a side radical at a phosphorus atom leads to the formation of polymers with a lower softening point (Fig. 7). The physical properties of the polymer are greatly influenced not only by the structure of the phosphonic and phosphoric acid derivatives, but also by that of the dihydroxy-compounds which participate in the polyesterification. The introduction of aromatic structures in place of aliphatic in the polymer chain sharply increases the glass point [156].

From what has been said earlier it is evident that the Taft equation is applicable to the hydrolysis and alcoholysis of phosphoric compounds, and these are the back reactions to polyesterification. It is known that the molecular weight of the polymer depends on the reaction rate, and the properties of the polymer (softening and melting points) are

TABLE 9. Softening point of copolymers of vinylphosphate esters and some vinyl-containing monomers, and their Taft constants [4,108].

Monomers	Proportion, %	σ^*_R	σ'_R	Softening point, °C	Reaction conditions
$(C_2H_5O)_2P(O)OCH=CH_2$	63.4				
$CH_2=CHR$	36.6				
$R=C_6H_5$		0.6	0.1	68	N_2, 4.93% Bz_2O_2, 80°, 42 h
$(C_2H_5O)_2P(O)OCH=CH_2$	64				
$CH_2=CHR$	36				
$R=CH_2OC(=O)$		2.00	0.35	110	N_2, 5% Bz_2O_2, 80°, 42 h
$(C_2H_5O)_2P(O)OCH=CH_2$	77				
$CH_2=CHR$	23				
$R=N\equiv C$		1.95	0.6	210—220	N_2, 6% Bz_2O_2, 80°, 42 h

§ σ' is the conjugation factor in σ values, which characterises the interaction between the substituents and the reaction centre (Taft's terminology for σ' is the resonance constituent of σ).

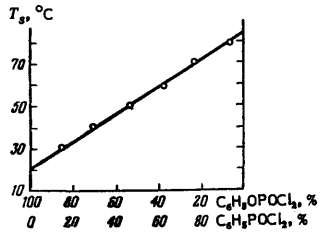


Fig.7. Softening points of mixed polyesters obtained from $C_6H_5POCl_2$, $C_6H_5OPOCl_2$, and hydroquinone.

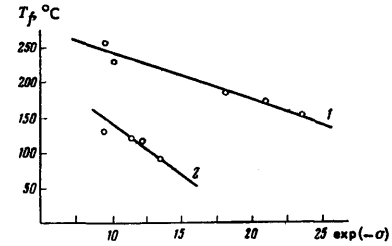
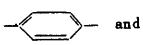
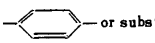


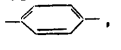
Fig.8. Dependence of the melting points of polymers with three P–C bonds on the constants 10 exp(-σ):
1) polyamides; 2) polyesters.

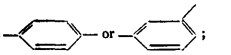
related to the molecular weight[162-163]. Therefore a relation between the Taft constants σ or 10 exp (-σ) and certain properties of polycondensation polymers is possible. Such a dependence can be traced by the example of phoryl resins, polymers with a lateral P–C bond, polymers with a P–N bond (polyureas and polyurethanes), and polymers with three P–C bonds (polyesters and polyamides)[103-112,115,125,151,153,160,161].

The conditions under which the reaction is performed have a great effect on the properties of the polymers; therefore they are best considered in groups of polymeric compounds obtained under almost identical conditions:

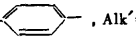
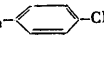
$-[-P(O)(OAr')OArO-]_n-$, where Ar =  and Ar' is substituted phenyl;

$-[-P(O)(Alk)OArO-]_n-$, where Ar =  or substituted *p*-phenylene and Alk = CH_3, C_6H_5, $(CH_3)_2N$;

$-[-P(O)(Alk)NHC(=O)NHArNH-]_n-$ and $[P(O)(Alk)NHC(=O)Ar'O-]_n-$, where Ar =  ,

Alk = C_2H_5, Ar' =  or ;

$[P(O)(Alk)ArC(=O)OAlk'O]_n$, where Alk = CH_3, C_2H_5, C_6H_5, Ar = , Alk' = $-(CH_2)_2-$, $-(CH_2)_4-$, $-(CH_2)_5-$, $-(CH_2)_6-$;

$[P(O)(Alk)ArC(=O)NHAlk'NH]_n$, where Alk = C_2H_5, C_6H_5, Ar =  , Alk' = $-(CH_2)_4-$, $-(CH_2)_6-$, $-(CH_2)_8-$, $-(CH_2-)_{10}$, , $-CH_2-$  $-CH_2-$.

Figs. 8 and 9 give data on the melting and softening points of various polymers as functions of 10 exp (-σ) and exp $[-(\Sigma\sigma + \Sigma E_S)]$ respectively, and show that for most of the substituents in the phosphorus-containing component or in the phosphorus-free component an increase in σ and a decrease in 10 exp (-σ) for the substituents corresponds to increases in the softening and melting points.

The term Σσ was calculated, using the additivity principle, from published data[1-4]. The phosphorus-containing polyamides are distinguished by higher melting points than the polyesters, but polyamides from aromatic diamines have higher melting points than polyamides from aliphatic diamines. The effect of parity on the properties of phosphorus-containing polyamides is retained in the aliphatic series. Furthermore, the change in melting and softening points is more gradual for polyesters and polyamides than for polyurethanes and polyureas. The melting and softening points for the series of phosphorus-containing polymers are greater when the functional groups are in the *para*-position. The softening point increases with the polarity and with a decrease in the steric factor of the substituent.

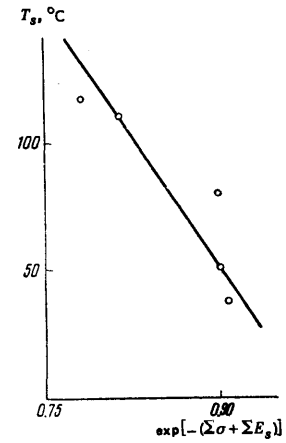


Fig.9. Dependence of the softening point of certain phoryl resins on the constant exp$[-(\Sigma\sigma + \Sigma E_S)]$.

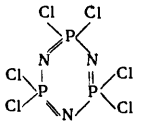
From the above it is evident that there is a relation between the Taft constants and certain properties of polymers, when the reaction proceeds under ordinary conditions. This has been confirmed repeatedly[164-166].

IV. PROPERTIES OF INORGANIC AND ORGANO-ELEMENTAL PHOSPHORUS-CONTAINING COMPOUNDS

Dichlorophosphazene, from which thermally stable and fire-resistant polymers are now produced, corresponds to a series of polymers of general formula $(PNCl_2)_x$, where x = 3, 4, 5, 6, 7, etc. The methods of preparing halogenophosphazenes and their derivatives have been described in many papers and reviews[167-184]; rather fewer works have been devoted to the structure of the halogenophosphazenes and their derivatives[176,184-191].

The cyclic structure of phosphazenes is retained in many reactions in which the chlorine atoms are replaced by other electronegative groups. However, such reactions relate mainly to trimeric and tetrameric chlorides (halides), since the higher polymers, for example, a mixture of composition $(PNCl_2)_{8-n}$ [where n may be large (Ed. of Translation)],

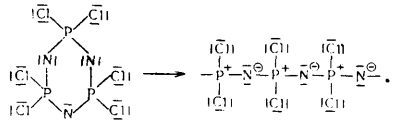
are comparatively inert. Chlorophosphazenes are less reactive in hydrolysis than acid chlorides. The lower chlorophosphazenes have a cyclic structure which ensures that the compound has a high stability:



The chlorine and phosphorus atoms are situated in planes perpendicular to the P_3N_3 ring, which is planar in both the trimer and tetramer [176].

To study the structure, the frequencies of the bending vibrations of the P–N bonds were measured. The electronegativity of the substituent greatly affects the frequency of these vibrations (it increases with the electronegativity). With the cyclic halogenophosphazenes there is the possibility of using *d* orbitals for the formation of π bonds [175], since the phosphorus atom has five electrons for four bonds formed from sp^3 hybrid orbitals, and a *d* orbital is left for the formation of a π bond. In this, the *p* orbital and the *d* orbital have different symmetry and for maximal overlap must alternate in sign:

With an increase in the fractional positive charge on the phosphorus its reactivity towards nucleophilic reagents is increased. Steric effects must also be considered. Thus the inter- and intra-molecular forces of interaction of large chlorine atoms have a marked effect on stability [176,184,186]. Consequently, the stability and reactivity of halogenophosphazenes and their derivatives are determined by the polar and steric factors of the substituent at the phosphorus atom. It is also known that phosphorus(V) derivatives having a group of low electronegativity form cyclic halogenophosphazenes (polymers) with difficulty. The polymerisation of halogenophosphazenes usually proceeds with cleavage of the ring:



Oily halogenophosphazenes have a linear structure. Such a chain consists on the average of ten $-N-PCl_2-$ groups,

and at their ends are $-N=PCl_3$ or $-\underset{|}{\overset{|}{P}}=NH$ groups.

The linear polymers based on chlorophosphazenes are unstable to moisture. The replacement of chlorine by a radical increases the moisture resistance slightly [178–185], the increase being greater the more electronegative the radical. Polymers obtained from halogenophosphazenes have high thermal stability (up to 350–500°).

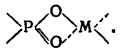
There have been some interesting studies of phosphinoborines and polymers based on them. Trimeric dialkylphosphinoborine has been studied in greater detail. The tetramers and high polymers which have been obtained are unstable and difficult to investigate. Phosphinoborines are hydrolysed by water only under very drastic conditions [192–195]. The reason for the chemical inertness lies in the nature of the covalent bond, which includes the 3*d* orbital of phosphorus [194]. The stability is also determined by the steric effects of the alkyl groups. Thus in the homologous series of alkylphosphinoborines — with substituents at boron of $(CH_3)_3P$, $(C_2H_5)_3P$, and $^i(C_3H_7)_3P$ — the stability falls to zero on account of the increasing steric hindrance and decreasing polarity of the substituents at the phosphorus atom [195]. Other investigators have also confirmed these facts [195–199].

Phosphorus- and silicon-containing polymers are also of interest [200–210]. They are obtained in the modification of hydroxyl derivatives of trimeric chlorophosphazene with chlorosilanes, in the reaction of phosphoric anhydrides or esters with derivatives of silanols, of phosphines with unsaturated silicon-containing compounds [200–202], and by other methods. Comparative data on the properties of monomers containing silicon and phosphorus are available. For example, it is noted that the more polar the substituent between silicon and phosphorus, the higher the melting point of the compound [205].

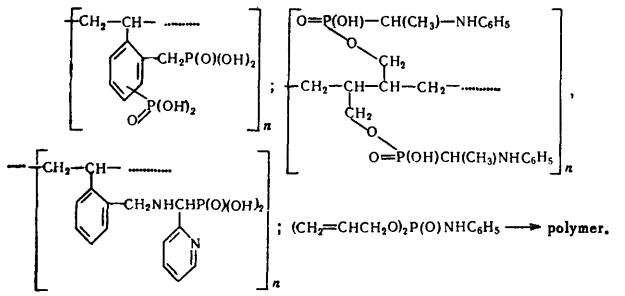
Polymers have been prepared containing phosphorus and selenium, titanium and phosphorus, tin and phosphorus, phosphorus and aluminium, and other neighbouring elements [211–214], but their properties have not yet been studied sufficiently.

The influence of the structure of phosphorus-containing monomers and polymers on salt formation and complex formation and on the properties of the compounds obtained has been studied [215–218]. Salt formation can be illustrated by the formation of salts of phenylphosphonic acid at definite pH in the medium [215].

Complex formation can proceed with monomers and polymers in the presence of $\rangle$PO(OH) groups, with the formation of monomeric or polymeric chelate complexes [216–218]. Thus, Kennard and his coworkers phosphorylated chloromethylated styrene cross-linked with divinylbenzene. The product forms with metal ions the four-dimensional chelate ring:



Analogous resins are obtained on the basis of allyl phosphates:



Resins of this type are used to separate copper, iron, and nickel ions, and partly for the separation of gold, palladium, and uranium ions. The activity of the resin in saltion to the metal ions changes in the following order:

$$Th^{4+} \text{ and } U^{4+} > UO_2^{2+} > Fe^{3+} > \text{rare earths} > H^+ > Cu^{2+} > Ba^{2+}.$$

The products formed as a result of complex formation have high thermal stability and strength [216]. When monomeric

complexes are formed, a change in the frequency of the bending vibrations of the $-\overset{|}{\underset{|}{P}}=O$ bond is possible, because in complex formation the following factors may affect the P–O bond. An increase in the charge on the metal ion and a decrease in its radius increase the deformation of the P^+-O^- bond. At the same time, on account of the shift of electrons from the *p* orbital to the *d* orbital a decrease in the back-bonding (Cotton's terminology) of O^--P^+ is possible, and together with this a reduction in the bond deformation. A shift of the $d\pi$ electrons of the metal to the *p* orbital of oxygen, from which the electrons are displaced to the vacant *d* orbital of phosphorus, makes possible an increase in the bending vibration frequency of the P–O bond[218].

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The available published information on the effect of the structure of phosphorus-containing compounds on their reactivity and physical properties have been collected in this article, using, where possible, quantitative and semiquantitative characteristics (the Hammett and Taft constants). It should be noted that the published data on this subject are far from adequate and their use is hindered by the variety of conditions under which they were obtained. The authors hope, however, that this material will be of use in solving the problems of the production of phosphorus-containing compounds of desired properties.

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